

INNOVATIVE WASTE MANAGEMENT TECHNIQUES FOR TREATMENT OF  
EFFLUENTS FROM IN-SITU FLUSHING PROCEDURES

By

CLAYTON J. CLARK II

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By

Clayton J. Clark II

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Chairman: Michael D. Annable

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Subsurface contamination with non-aqueous phase liquids (NAPL) is regarded as one of the most urgent problems in the environmental field today. Removal of contamination by pump-and-treat technology has been often employed to remediate contaminated sites, but has been seen to be an inefficient process. Using surfactants and cosolvents has been reported to increase the efficiency of pump-and-treat processes used in remediation. However, little investigation about the treatment of the effluent produced by enhanced pump-and-treat procedures has been conducted. The goal of this research was to examine the effectiveness and efficiency of waste management techniques that could be implemented in treating effluents from in-situ flushing remediation procedures. These techniques included intermediate treatment measures (phase separations) and

previously not fully explored innovative destructive techniques (zero-valent iron and sonication). The research focused on management of effluent from a surfactant/cosurfactant flush of a Superfund site at Hill AFB, Utah, and potential effluents that might result from a cosolvent flush of soil contaminated with tetrachloroethylene (PCE). Phase separation was used to reduce the amount of high-level waste that required expensive destruction by incineration. Zero-valent iron ( $\text{Fe}^0$ ) and sonication were examined as methods to degrade PCE in aqueous solutions. Phase separations by salt addition, elevated temperatures, and a combination of both resulted in most of the NAPL, surfactant, and hydrophobic components partitioning into separated organic-rich phases. Salt addition at elevated temperatures reduced the volume of NAPL-dominated waste by over 95%, while >98% of the mass of target hydrophobic components and 90% of the COD load partitioned into the organic-rich phase after separation. Degradation of PCE was found to result in pseudo first-order rate functions both in the presence of  $\text{Fe}^0$  and due to applied sonication. Increasing cosolvent (ethanol) fractions in the solutions decreased the adsorption of PCE to the iron surfaces, and, therefore, decreased PCE degradation rates in the presence of  $\text{Fe}^0$ . Increasing ethanol fractions and initial PCE concentrations in aqueous solutions decreased degradation rates of PCE due to sonication. These waste management techniques could be used to reduce total cost of waste treatment, thereby, improving the efficiency of remediating hazardous waste sites.

## CHAPTER 1 INTRODUCTION

Over the past twenty years, great interest has been shown in the area of environmental remediation of hazardous-waste contaminated sites. In 1980, the United States Congress passed the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), requiring cleanup of abandoned hazardous-waste sites, and in 1984, it amended the Resource Conservation and Recovery Act (RCRA) to require cleanup of contamination at active sites (Gillham, 1996). The need for newer, more efficient technology is driven by the large number of polluted sites across the country; approximately 14,900 sites are presently within the Department of Defense (DOD), and more than 1,200 Superfund sites are on the National Priorities List (NPL). The exploration of alternative technology is needed to supercede conventional remediation and destructive techniques. In 1994, approximately 20% of the Environmental Protection Agency's (EPA) cleanup decisions at Superfund sites involved the use of innovative technologies. The creation of the Superfund Innovative Technology Evaluation (SITE) program by the EPA also indicates a willingness to explore and scale up emerging technologies (Hua and Hoffman, 1997).

Subsurface contamination with non-aqueous phase liquid (NAPL) wastes constitutes a large portion of these contaminated sites and is regarded by many as one of

the most urgent problems in the environmental field today. Due to the potential to contaminate groundwater, the need to remediate sites where subsurface NAPL contamination is present is a priority for scientists and engineers alike. As a consequence of the emergence of groundwater remediation as an environmental priority, it is not surprising that the initial and most commonly used methods of cleanup rely heavily on existing technologies based on aquifer hydraulics. Pump-and-treat technology (see Figure 1-1) is often employed to remediate contaminated sites by introducing clean water to the contaminated area, and then removing the water which has solubilized (Figure 1-2) the contaminant at residual levels (Keely, 1996). Figure 1-1 shows a schematic of an enhanced pump-and-treat technology with a hydraulically isolated test cell similar to the one used in Hill AFB, Utah in 1996. Over the period 1982 to 1992, at the hazardous waste sites with groundwater contamination for which cleanup agreements had been established under CERCLA, pump-and-treat remediation was specified for 73% of the locations (Gillham, 1996). However, from an analysis of 77 sites, 69 had not yet achieved the cleanup objectives. Similar reports from other sites added to the perception that conventional pump-and-treat technology alone is not an effective method for groundwater remediation.

Reasons listed for the poor performance of pump-and-treat systems include incomplete characterization of the zone of contamination, diffusion of contaminants in low permeability zones, hydrodynamic isolation in subsurface zones, incomplete removal of the contaminant source zone, desorption of contaminants from the solid phase and geologic heterogeneity, and liquid-liquid partitioning of immiscible contaminants

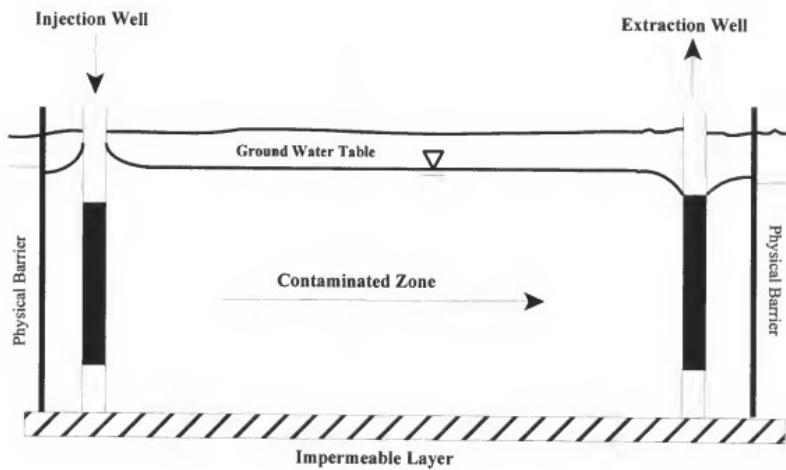


Figure 1-1 Schematic of general pump-and-treat configuration

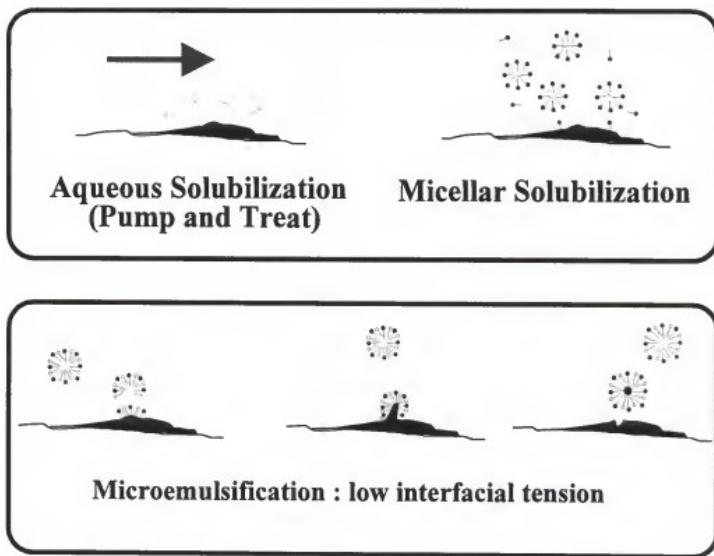


Figure 1-2 Microscopic view comparing types of solubilization (Jawitz et al., 1997)

(Gillham, 1996; Keely, 1996). Due to such limitations of conventional pump-and-treat technology, there is an incentive for developing alternative methods of treatment. In-situ flushing, which involves the addition of chemicals to the pumping water to enhance removal of NAPL contaminants, has experienced recent success for remediation of NAPL source zones (Clarke et al., 1993; Martel et al., 1993; Jawitz et al., 1997; 1998). The most often used chemical agents, surfactants and cosolvents, have been proven by many investigators to facilitate the remediation of aquifers contaminated with NAPLs in a more timely manner than pump-and-treat technology with water alone (Sabatini et al., 1996; Chevalier et al., 1997; Rao et al., 1997).

Both surfactants and cosolvents act to improve NAPL removal from porous media by mobilization or enhanced solubilization. Mobilization occurs with the reduction of the NAPL-water interfacial tension and is usually discouraged for DNAPL (dense non aqueous phase liquids) sites, since it may cause uncontrolled migration of DNAPL to previously uncontaminated regions of the aquifer. When a surfactant is added to an aqueous phase, the organic interior of micelles acts as an organic pseudo phase into which hydrophobic contaminants can be partitioned. This phenomenon is known as solubilization (West and Harwell, 1992). Solubilization of NAPL into the aqueous phase is enhanced by the reduced polarity of the flushing solution compared the groundwater at the site (Figure 1-2). This reduced polarity leads to partitioning of the residual NAPL into the flushing solution away from the relatively polar resident groundwater in the porous media of the subsurface environment. Each of these phenomena are used to improve the efficiency of remediation processes by reducing the amount of water, time,

and cost required to fully decontaminate a hazardous waste site.

### Surfactant Flushing

Surfactants are surface active agents which accumulate at the interface, and, therefore, alter the surface tension of a liquid. Surfactant molecules generally consist of both a hydrophobic and hydrophilic portion. The hydrophobic portion is usually a hydrocarbon chain, while the hydrophilic portion is an ionic or polar head, or a polyethoxyethylene chain (Rosen, 1989; Palmer and Fish, 1996). Surfactants are classified according to the character of the head or hydrophilic portion of the molecule. The head group may carry a negative charge (anionic), a positive charge (cationic), both negative and positive charges (zwitterionic), or no charge (nonionic). These surfactants generally concentrate at the polar-nonpolar interfaces, and as enough of the molecules come together they form surfactant aggregates known as micelles. A micelle can be made up of hundreds of surfactant monomers (Figure 1-2). The threshold concentration at which micelles begin to form is known as the critical micelle concentration (CMC). Once the CMC has been surpassed in solution, any surfactant added to the aqueous solution will not increase the number of monomers in the solution, but instead will contribute to the formation of additional micelles (Rosen, 1989). The interior of a micelle can be described as a pseudo-oil phase. Organic compounds preferentially partition into the interior of the micelle, thereby increasing the solubility of the organic in a surfactant solution relative to its water solubility (Wade et al., 1978). The effectiveness of surfactant flushing is based on this ability of surfactants to solubilize extremely

hydrophobic compounds into a bulk aqueous phase solution. The partitioning of an organic contaminant between the aqueous phase and micelle is defined by a solubilization or partition coefficient ( $K_m$ ). This quantification of enhanced solubility was expressed by Hasegawa et al. (1997) and Pennell et al. (1997) as:

$$K_m = X_m / X_a$$

where  $X_m$  is the mole fraction of the organic contaminant in the micellar phase,  $X_a$  is the mole fraction of the contaminant in the water phase.

Surfactant flushing has experienced recent success in remediation of NAPL contaminated subsurface environments (Sabatini et al., 1996; Clarke et al., 1993; Jawitz et al., 1998). Once used primarily by the petroleum industry for oil recovery (Bansal and Shah, 1978; Wasan et al., 1978), surfactants are now used to extract NAPL compounds from the subsurface for remediation purposes. Surfactants are used in various forms in remediation procedures, one such form is in microemulsions. Microemulsions are thermodynamically stable, transparent dispersions containing two immiscible liquids with particles of 0.01-0.1  $\mu\text{m}$  diameter (Hu and Prausnitz, 1988; Rosen, 1989). With an interfacial tension close to zero, microemulsification easily solubilizes immiscible fluids into single phase solutions (Figure 1-2). This property is very effective in removing NAPL from subsurface aquifers during in-situ flushing processes. Healy and Reed (1977) showed the effects of immiscible microemulsion displacement of residual oil and water and how it related to various interfacial tensions in a surfactant solution. Among other things, Healy and Reed (1977) concluded that as the hydrophobic chain length increased, oil recovery improved because of increased solubility of oil in the

microemulsion. Martel et al. (1993) concluded that the water solubility of nonionic surfactants depend on the length of the ethoxylated chain. The longer this chain, the higher the water solubility of the surfactant.

Alcohols have been used in conjunction with surfactant solutions as well. The main reason for adding alcohols to microemulsions is to balance commercial surfactants' affinity between oil and water by acting as cosurfactants (Strey and Jonströmer, 1992). Sarbar et al. (1984) stated that a combination of both a surfactant and a cosurfactant stabilized an emulsion mixture and acted as wetting agents in their extraction of bitumen from tar sands. Sarbar et al. (1984) also noted that both components were recovered by water flushing after contaminant removal. Also using a combined surfactant/cosurfactant mixture, Jawitz et al. (1998) described the remediation of a hydraulically isolated test cell (Figure 1-1) at Hill AFB, Utah. With the aid of the surfactant (Brij 97, 3.0%) and cosurfactant (pentanol, 2.5%) solution, approximately 95% of the most prevalent NAPL contaminants were removed by the surfactant flood conducted at the site.

Comparing the various types of surfactants, nonionic surfactants seem to be favored in subsurface cleanup procedures due to their higher solubility in water and organic solvents; and their lack of ionic charge generally causes them to neither repel from or adsorb to solid surfaces such as soils or metals (Rosen, 1989). Kibbey and Hayes (1997) discussed the multi-component analysis of ethoxylated nonionic surfactants and the difficulties it might entail. It was further stated that nonionic surfactants are used in subsurface contaminant remediation due to their high solubilization capacities, nonreactivity with multivalent cations, and high biodegradability. Kibbey and Hayes

(1997) relayed that generally surfactants with fewer ethoxylate units are smaller, more hydrophobic, have lower CMCs, and are more biodegradable than those with greater numbers of ethoxylate units.

Pennell et al. (1997) also discussed the use of ethoxylated nonionic surfactants in solubilization of frequent subsurface contaminants. Pennell et al. (1997) discussed the attractiveness of nonionic surfactants in subsurface remediation applications, such as their lack of sensitivity to background electrolyte concentrations in soil and groundwater.

As previously mentioned, Jawitz et al. (1998) reported successful results in using a ethoxylated nonionic surfactant based microemulsion for removal of NAPL contamination in a field test study. Both the injected precursor solution, including surfactant (Brij 97), cosurfactant (pentanol), and the extracted fluid with solubilized NAPL constituents were encapsulated into a single-phase microemulsion (SPME) solution (Rhue et al., 1999). The resulting microemulsion has been described as a Winsor Type I mixture by Lake (1989), in which the micelles in the solution more readily solubilize hydrophobic components into an aqueous system.

Surfactants in microemulsion systems have been shown to elevate solubilization of hydrophobic components into aqueous bulk solutions. Their enhanced solubilization capacity has shown them to be especially useful in removing NAPL contaminants from subsurface systems. However, little work has been done in respect to treatment or management of microemulsion effluents produced by in-situ flushing experiments. Utilizing methods such as phase separation of waste components and recycling materials could aid in improvement of the overall efficiency of a site remediation process.

### Cosolvent Flushing

Cosolvent flushing involves the addition of water-miscible organic cosolvents (alcohols) to injection water to increase the contaminant solubility. This is based on the fact that many alcohols are miscible in both water and NAPL, therefore alcohols can increase the aqueous solubility of many slightly soluble organic compounds. A log-linear increase in contaminant solubility has been reported by Rao et al. (1985), Fu and Luthy (1986a), Fu and Luthy (1986b), Rao et al. (1990) and Augustijn et al. (1994). Increasing the contaminant solubility simultaneously reduces contaminant sorption, reduces the retardation factor, and increases sorption mass transfer rates (Rao et al., 1990; Wood et al., 1990). At high cosolvent contents, usually at volume fraction >70% for lower alcohols (such as methanol) and >30% for higher alcohols (e.g., butanol), complete mobilization and immiscible displacement of residual NAPLs is possible (Rhue et al., 1994). This is due to significant lowering of the NAPL-water interfacial tensions, and to ganglia swelling upon preferential partitioning of the cosolvent into the NAPL phase.

The major advantage of the cosolvent flushing technique lies in the elevated solubility and mobilization of contaminant in the mixed solvent, as compared to flushing with water. The enhanced solubility can be quantified by the cosolvency power (Rao et al., 1985; 1990; 1991):

$$\sigma_{s,c} = \log [S_{s,c} / S_{s,w}]$$

where  $\sigma$  is the cosolvency power and  $S$  is the solute (subscript s) solubility (mg/L) in neat cosolvent (subscript c) or pure water (subscript w). The cosolvent flushing method has advantages over other enhanced liquid extraction techniques because the extraction

cosolvent is not sorbed by the aquifer matrix, and is easily removed from the system by water flushing; any residual cosolvent remaining in the system is also susceptible to biodegradation. Also, NAPL solubilization during cosolvent flushing is apparently not subject to mass-transfer limitations (Sillan et al., 1998), as is the case with surfactant flushing (Pennell et al., 1997). However, cosolvent flushing does not generally remove as much NAPL as surfactant flushing (Rao et al., 1997; Jawitz et al., 1998) as can now be proven with the aid of partitioning tracer tests (Jin et al., 1995; Annable et al., 1998a; Annable et al., 1998b).

The use of cosolvent flushing as an effective method for treatment of contaminated soils has been documented in both laboratory and field settings. Wood et al. (1990) reported that equilibrium sorption constants exhibited an inverse, log-linear dependence on the volume fraction of methanol in the mixed solvent. It stated that this dependence corresponded closely to the increase in solute solubility with the addition of cosolvent (Wood et al., 1990). Augustijn et al. (1994) recorded the improving removal of naphthalene and anthracene with increasing methanol cosolvent fractions. Augustijn and co-workers (1994) concluded that high cosolvent fractions are most efficient in the elution of contaminants.

Imhoff et al. (1995) reported increased solubility of PCE in effluent when cosolvent solution was introduced as the influent solution. A cosolvent mixture of 60% methanol/ 40% water was found to increase PCE solubility in water from 225.4 mg/L to 8986 mg/L, which decreased amount of influent solution needed to remove PCE from soil. Rao et al. (1997) reported an average >85% mass of the target NAPL contaminants

removed by cosolvent flushing at a field site at Hill AFB, Utah. This cosolvent mixture, which consisted of 70% ethanol, 12% *n*-pentanol, and 18% water, effectively removed components as large as *n*-decane and naphthalene.

### Waste Management

The use of surfactants and cosolvents have been reported to increase the efficiency of pump-and-treat processes with remove NAPL contaminants from soil. This efficiency is based on the fact that with these chemical additives, less water and time is required to remediate these hazardous waste sites. However, little has been said about the need to handle the effluent produced by these enhanced pump-and-treat procedures.

Unlike conventional pump-and-treat measures, the effluent produced by these remediation efforts is not water with contaminants at or below aqueous solubility limits. These effluents will contain large fractions of NAPL, alcohols, and surfactants which must be handled as hazardous waste once removed from the subsurface. In the past, these effluents were most often treated by expensive processes such as air stripping, vacuum steam stripping, micellar enhanced ultrafiltration, carbon adsorption, or biotreatment. Generally, these processes would transfer the contaminant from one form to another until a terminal destructive process was implemented. Most often, for high level wastes, this terminal process would be incineration (Rao et al., 1997; Jawitz et al., 1998). Perdek (1997) reported that incineration can constitute between 45 and 75% of the total cost of remediating a contaminated site, which shows that the cost of incineration is not insignificant. Incineration cost, in addition to cost of the earlier mentioned treatment

processes, can make the waste management portion of a remediation process the most financially challenging. Taking into account that there are an estimated 300,000 to 400,000 hazardous waste sites in the U.S. and on the order of \$750 billion could be spent for cleanup over the next thirty years (Gillham, 1996), cost of waste management is a major factor in the arena of site remediation now and in the years to come.

To assist in reducing site remediation costs, new waste management technologies could be utilized in decreasing the costs of treatment of waste effluents. These technologies could take the form of intermediate treatment measures or adoption of newer destructive techniques. Employment of intermediate waste handling procedures, such as phase separation, can reduce the amount of high level waste that would require expensive destruction by incineration (Clark et al., 1997). Additionally, innovative destructive technologies, such as zero-valent iron treatment and sonication, could be further explored to determine their effectiveness in treating waste effluents from in-situ flushing procedures. Investigating the effectiveness and efficiency of such treatment options and how they might be implemented is the basis for this research.

#### Research Objectives and Organization

The main goal of this research was to determine the effectiveness and efficiency of waste management techniques that can be implemented in the treatment of effluents from in-situ flushing procedures. The research focuses on effluent taken from a surfactant/cosurfactant flush at Hill AFB, Utah (Figure 1-3), and on effluents that might be attained from cosolvent flushing of a soil contaminated with PCE.

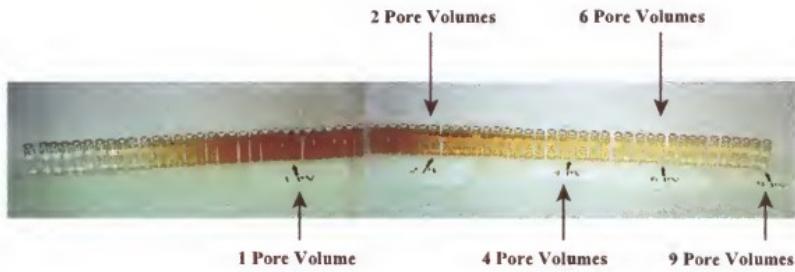


Figure 1-3 Single phase microemulsion (SPME) effluent samples taken from the Hill AFB, Utah, surfactant/cosurfactant flushing experiment

Research results in this dissertation are divided into seven chapters. Chapter 2 presents the application of an intermediate treatment step in handling a SPME waste produced from a surfactant flush. This intermediate treatment includes the addition of an electrolyte (salt) to the SPME to induce phase separation. The theory, methodology in field and laboratory sampling, and results based on GC (gas chromatography) and COD (carbon oxygen demand) analysis of the separated phases are presented. Also included is an analysis of the potential cost of implementing this procedure on the field scale.

Chapter 3 examines the application of elevated temperatures as a potential intermediate treatment step in the managing of SPME waste effluent produced by the surfactant/cosurfactant flush conducted at Hill AFB, Utah. This chapter includes the theory, procedures, and analysis of the immiscible phases as functions of temperature separation. The effects of mass and volumetric partitioning based on applied temperature are also presented in this chapter.

The combined effect of salt and temperature on the effluent of the SPME flush is presented in Chapter 4. As in Chapters 2 and 3, theory, procedures, and analytical results based upon GC and COD tests are presented as functions of added salt at elevated temperatures in this chapter. Both volumetric and mass analyses conducted on the separated phases are discussed in this chapter as well.

Chapter 5 investigates the ability of zero-valent iron to degrade PCE at concentrations above aqueous solubility limits in aqueous solutions which contained cosolvents. The degradation capacity of various types of iron surfaces are evaluated over a range of cosolvent fractions. The degradation rate constants, PCE half-lives, and

sorption isotherms are presented for various conditions to support deductions given in this chapter. Degradation by-product analysis is also presented in this chapter.

Chapter 6 presents the technique of sonication utilized to degrade aqueous solutions containing PCE over a range of cosolvent fractions. Theory and methodology for this procedure are explained in this chapter. Degradation rate constants, half-lives, and energy efficiencies are provided to support the conclusions made based on this process.

## CHAPTER 2

### SUBSURFACE MICROEMULSION WASTE REDUCTION BY ELECTROLYTE ADDITION

#### Introduction

Subsurface contamination with non-aqueous phase liquid (NAPL) wastes is regarded by many as one of the most urgent problems in the environmental field today. Due to the potential to contaminate groundwater, remediation of sites contaminated with NAPL is at present a priority for scientists and engineers alike. In-situ site remediation approaches have had growing success in removing subsurface contamination (Clarke et al., 1993; Martel et al., 1993; Jawitz et al., 1998). The addition of chemical agents to water that is flushed through the subsurface improves the removal efficiency of hydrophobic contaminants from the soil. These chemical agents, commonly known as surfactants and cosolvents, have been proven by many investigators to facilitate the remediation of aquifers contaminated with NAPLs in a more timely manner than can be achieved with pump-and-treat technology involving flushing water alone (Sabatini et al., 1996; Chevalier et al., 1997; Rao et al., 1997).

An in-situ remediation technology evaluated at Hill AFB, Utah involved flushing the contaminated aquifer with a remedial fluid (surfactant-cosurfactant enriched water) to microemulsify the multi-component NAPL, and then to miscibly displace the microemulsion. In this study, both the injected precursor solution, including surfactant

(Brij 97, 3.0%) and cosurfactant (pentanol, 2.5%), and the extracted fluid with solubilized NAPL constituents were encapsulated into a single-phase microemulsion (SPME) solution (Rhue et al., 1997; Rhue et al., 1999; Jawitz et al., 1998). Treatment of this waste by incineration costed nearly \$1.73/gallon based on upon costs provided by the consulting firm working at the site (CH2M Hill, 1997). Recognizing that the waste volume produced from the surfactant flushing in this study was approximately 20,000 gallons, disposal and treatment of the waste fluids generated during the in-situ flushing can be a major cost element, especially when scale up from the pilot-scale testing to full-scale site remediation is being considered.

Due to these high treatment costs, alternative waste management approaches must be investigated. The focus of these treatment processes may include reduction of the overall cost of the project and management of the residual waste collected during site remediation. The preferred final phase for these flushing technologies is to either dispose of the waste efficiently or recycle the chemical additives, such as the surfactant, for reuse. Usually, this requires some extensive treatment processes such distillation, steam stripping, or filtration before a final disposal process like incineration is employed. It has been previously reported that incineration can constitute between 45 and 75% of the total cost of remediating a contaminated site (Perdek, 1997). In our research, off-site incineration of all of the waste fluids generated would be perhaps the simplest, but also the most expensive, option at approximately \$1.73 per gallon, as previously mentioned. The costs of waste fluids treatment and disposal through the Hill Air Force Base (UT) Industrial Waste Treatment Plant (IWTP) are estimated at a total of about \$0.002/gallon. Costs associated replacement of the activated carbon used up at the IWTP are not

included in this estimate. To employ the less expensive IWTP rate, intermediate treatment steps could be employed to transform the SPME, or at least a large percentage of it, into a solution amenable to IWTP disposal. This research focuses on an inexpensive, yet effective, intermediate step of waste treatment. Addition of an electrolyte may be used to reduce the amount of waste that requires treatment, disposal, or the amount of work needed to recycle it. Also, reduction of costs incurred for energy required or treatment should reduce the total expenditures for waste treatment after site remediation, thereby improving overall project cost efficiency.

The purpose of this experiment was to examine the intermediate treatment process of adding an electrolyte (NaCl) to a single-phase microemulsion effluent from a surfactant/cosurfactant flushing test conducted at a field site. The addition of salt acts to separate the effluent SPME (Winsor Type I) into two thermodynamically, immiscible phases which include a lower aqueous phase and an upper oil-rich phase. In this separation, all or most of the NAPL, surfactant, and cosurfactant are partitioned into a hydrophobic upper phase. As a result, a significantly smaller volume of waste saturated with NAPL and additives would be produced. Since the volume of waste to be treated by a relatively expensive processes such as incineration would be reduced, the financial expenditures for treating this waste would also be reduced. The hydrophobic phase may also be treated as a fuels-grade waste for disposal by incineration, which would be less expensive than similar treatment for the total SPME effluent not meeting fuels grade specifications. The remaining aqueous phase could be disposed of and treated as industrial wastewater, which is generally a much less expensive option than is incineration. Since, the addition of NaCl can decrease the volume of NAPL for

incineration, the total cost of site remediation can be drastically reduced.

The objectives of this experiment were: 1) to investigate NaCl efficiency in effectively separating the field generated SPME; 2) to investigate the partitioning of the NAPL into the separated organic and aqueous phases dependent upon the NaCl concentration; and 3) to conduct a preliminary cost analysis of possible intermediate waste treatment by addition of NaCl.

### Background

The effluent SPME is the result of surfactant flushing of an isolated subsurface test cell at Hill AFB, Utah in an field experiment described by Jawitz et al. (1998). A detailed discussion of the field site including its historical and geophysical characteristics can be found in a report produced by Montgomery Watson, Inc. (1995). The hydraulically isolated test cell and the instrumentation included therein used in this experiment has been previously described (Rao et al., 1997; Jawitz et al., 1998; Annable et al., 1998b). The flushing solution consisted of a surfactant polyoxyethylene-(10)-oleyl-ether (trade name Brij 97) and n-pentanol as the cosurfactant. This microemulsion precursor solution, mixed at 3.0% by weight of Brij 97 and 2.5% by weight n-pentanol, was developed in the work conducted by Rhue et al. (1997; 1999). After flushing through the surficial aquifer, the SPME consisted of not only the surfactant solution, but also, the complex NAPL mixture characterized by Rao et al. (1997). Encapsulated in the microemulsion, the solubilized NAPL remains in the thermodynamically stable solution. The resulting microemulsion has been described as a Winsor Type I mixture by Lake (1989), in which the micelles in the solution more readily solubilize hydrophobic

components into an aqueous system. In the case of this field experiment, the waste effluent contained the solubilized hydrophobic NAPL in a water-miscible SPME solution.

The addition of salt acts to invert the system by making the NAPL less soluble in the aqueous phase, causing separation into two immiscible phases. In a Winsor Type I system, the interfacial tension between the immiscible fluids is nearly zero, which results in the NAPL being easily solubilized into the surfactant micelles. Salt reduces the solubilization capacity of the micelles in the microemulsion, which increases the interfacial tension between the immiscible fluids. The result is the separation of the immiscible fluids into layers based on the density differences. The upper organic phase consists of lighter-than-water hydrophobic components, while the bottom phase is primarily composed of hydrophilic, water-soluble components.

Due to its thermodynamic stability, breaking the microemulsion would mean "acting" on the solution, since it will not separate on its own. Adding an electrolyte has a definite effect on the solubility of organic compounds in water (Kahlweit et al., 1984; 1985; Wilcoxon, 1990; Kunieda and Nakamura, 1991; Kabalnov et al., 1995). The addition of certain inorganic salts may serve to decrease or increase the water solubility of organic solutes. Most salts decrease the solubility of hydrophobic organic components in water, which is referred to as the "salting-out" effect; while a few (NaI, NaClO<sub>4</sub>, NaSCN) increase solubility and produce a "salting-in" effect (Kabalnov et al., 1995). The focus of this study was the salting-out of or the decrease in the solubility of the hydrophobic components contained in the effluent microemulsion. The salting-out strength of anions have been defined by the Hoffmeister series (Kabalnov et al., 1995):



The use of NaCl in this research is based on its stability, ease of transport, and, most importantly, its low cost.

Kabalnov et al. (1995) reviewed the two theories surrounding the explanation of the Hofmeister series. One interpretation deals with the salting-out and salting-in phenomena at the interfacial boundary between the water and the organic solute. As the salt adsorbs or desorbs at the interface, a change in the free energy of the solute results in a modification of the phase equilibrium. The second theory suggests that salts effect the "solvent quality" of the water, and models brine as a pseudocomponent. Also, anions listed in (1a) are referred to as "structure makers", while those in (1b) are known as "structure breakers". Neither theory has been universally accepted, and presently, this controversy remains unresolved. Kabalnov et al. (1995) and Wilcoxon (1990) support the former explanation, and Kabalnov et al. (1995) stated that the phase behavior for the nonionic microemulsions is based at the interface and is due to the salt adsorption and depletion at the microemulsion monolayer. This theory led to an analogy of adsorption on a solid sorbent from the coexistent aqueous solution. Further, it was stated that "lyotropic" salts, those with (1a) anions, were shown to make water a more polar solvent, whereas the (1b) anions formed "hydrotropic" salts which oppose this trend (Kahlweit et al., 1984; Kahlweit et al., 1985). Kabalnov et al. (1995) concluded that lyotropic salts cause a depletion of the microemulsion phase in salt, while hydrotropic salts cause the microemulsion phase to be enriched in salt.

Rosen (1989) mentioned that separation or "salting out" of the hydrophobic groups in the aqueous solvent is a product of lowering the CMC (critical micelle concentration) which favors micellization. The work needed to create the volume in water required to accommodate a nonpolar solute is changed in electrolyte solution because of water-ion interactions. As the work is increased by the introduction of electrolytes (neutral), the activity coefficient of the solute increases and the organic solute coalesces in a separate phase away from the aqueous phase.

### Materials and Methods

Liquid samples were taken periodically from the combined effluent of the three extraction wells from the surfactant/alcohol flushing experiment in test-cell 8 located at Operable Unit-1 (OU-1) at Hill Air Force Base, Utah. Samples of the composite waste fluids were taken from the effluent from the entire flushing experiment, and also the first pore volume displaced.

### Laboratory Experiments

To compare the effects of differing concentrations of salt, NaCl at varying weight percentages (0.1 - 20% by weight) was added to 10 mL volumes of the effluent SPME in centrifuge tubes (KIMAX®). Following the addition of the salt, the 10 mL volumes were centrifuged at a moderate speed of 2.0 rev/min for 15 minutes to separate the microemulsion. After phase separation, an aliquot of the upper organic layer was diluted (1:10) in methylene chloride ( $\text{MeCl}_2$ ). The  $\text{MeCl}_2$  solution and the aqueous phase were both analyzed by GC-FID for target analytes as well as for pentanol. In the extraction procedure, the  $\text{MeCl}_2$  and upper separated organic phase were batch extracted and

allowed to equilibrate on a rotary shaker for 2 days (Chen et al., 1996).

To evaluate the phase separation efficiency of the varying salt concentrations, volumes of the separated organic and aqueous phases were measured based on the graduations on the individual centrifuge tubes. From these values, ratios of aqueous to organic phase volume fractions of the separated SPME were used to numerically compare the effectiveness of various salt concentrations on the field-generated SPME effluent.

#### Field Experiment

To evaluate the proposed treatment process in the field, a 25 L glass carboy and a 208 L steel drum were both filled periodically over the duration of the in-situ flushing experiment conducted by Jawitz et al. (1998). Based on the estimated 20,000 gallons of waste fluids to be produced during the in-situ flushing test, proportional volumes were added to the two containers at various times during the field experiment to produce smaller versions of the larger effluent waste tank. Filling the 25 L and 208 L containers periodically over the length of the experiment helped to ensure relatively consistent compositions between the these containers and the large waste tank containing the fluids.

Phase separation in the 25 L carboy was achieved by slowly adding salt over a period of about 3 minutes to achieve a concentration of 11 wt.%, then mixing for three 5 minute intervals. Phase separation was complete within 6 hours. Samples were taken from three different levels in the glass carboy: the top oil layer, the bottom of the aqueous phase, and the middle of the aqueous phase. Each level was analyzed by GC-FID to determine composition of the target analytes and pentanol according to the protocol suggested by Rhue et al. (1997). The procedure was similar for the 208 L drum, in which 11% by weight of salt was slowly added over a 30 minute period. The only deviations

included sampling twice from the middle of the separated system, 1 and 2 feet below the surface, and mixing for 10 minute intervals.

A Perkin-Elmer Autosystem Gas Chromatograph (GC), equipped with a Flame Ionization Detector (FID) and a DB-624 column, was used to analyze the microemulsion waste and the MeCl<sub>2</sub> dilutions of the organic phases for surfactant residuals, pentanol, and target NAPL analytes. The target analytes, selected by Rhue et al. (1997), included p-xylene, 1,2,4-trichlorobenzene, 1,2,4-trimethylbenzene, n-decane, n-undecane, n-dodecane, and n-tridecane.

Chemical oxygen demand (COD) tests were conducted based on the EPA approved (Federal Register, 1980) Reactor Digestion Method 8000 found in DR/2000 HACH Spectrophotometer Handbook with HACH High Range Plus COD Reagent (Loveland, CO). The high level wastes were also analyzed with colorimetric determination with a Milton Roy Spectronic 21D Spectrophotometer.

### Results and Discussion

#### Laboratory Test

In the lab experimentation, salt concentration was varied over a range of weight percentages to test the effectiveness and efficiency phase separation when salt was added to SPME effluent. The effectiveness would be evaluated based on the ability of salt to produce phase separation, while its efficiency was based on how little was required to achieve the level of phase separation desired. The SPME samples were taken during the elution of the first pore volume and from the composite volume of the total SPME effluent. In addition to evaluating the effectiveness of the salt addition, the cost

efficiency was also studied based on the laboratory and the field-generated data.

The SPME effluent from the in-situ flushing test was analyzed by GC-FID for the target analytes. The concentrations of these target analytes were scaled to the zeroth moment to show that the composition of the SPME effluent was relatively constant over the duration of the in-situ flushing experiment (Figure 2-1). The zeroth temporal moment ( $M_0$ ) is proportional to the total mass of the analyte extracted and detected in the total effluent volume and is calculated by the following equation (Valocchi, 1985):

$$M_0 = \int_0^{\infty} c dt$$

The data displayed in Figure 2-1 provided evidence that there was minimal preferential partitioning of the different compounds over the length of the experiment. Consequently, the NAPL constituent concentrations in the waste effluent over the flushing experiment changed only due to the decrease in the total NAPL amount, but the relative concentrations of the target analytes remained consistent. Pentanol concentration in the effluent, scaled to the influent concentration of 2.5%, is also displayed in Figure 2-1.

This analysis was repeated on the organic-rich phase after phase separation due to addition of 11 weight percent of salt to the SPME effluent (Figure 2-2). Just as in Figure 2-1, the composition of the analyzed phase was relatively constant over the duration of the flushing experiment. Therefore, phase separation by salt addition did not promote preferential partitioning of components into the organic phase. Also, the organic-rich phase partitioning of components was not a function of the amount of NAPL removed, but rather it was relatively homogeneous in composition based upon analyzed target

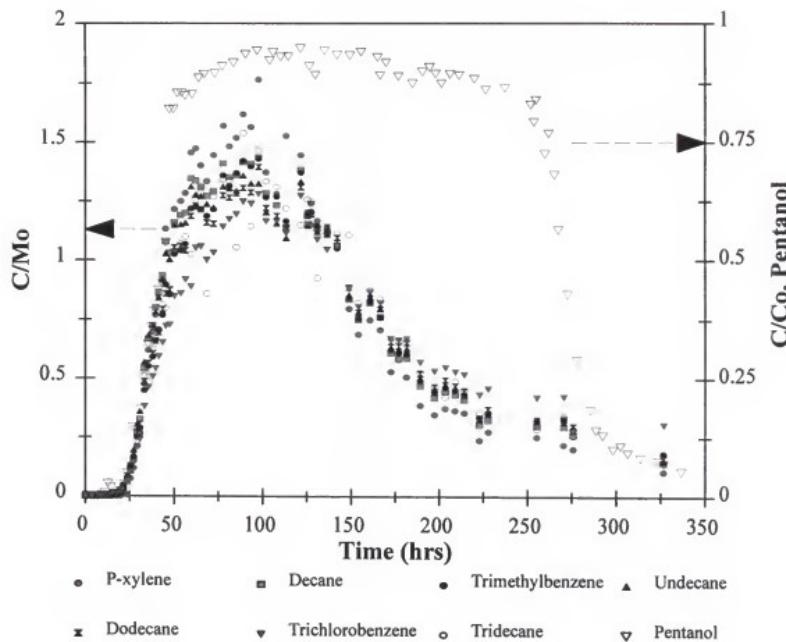


Figure 2-1 Elution of target analytes over duration of the single phase microemulsion (SPME) flushing experiment in Hill AFB, UT

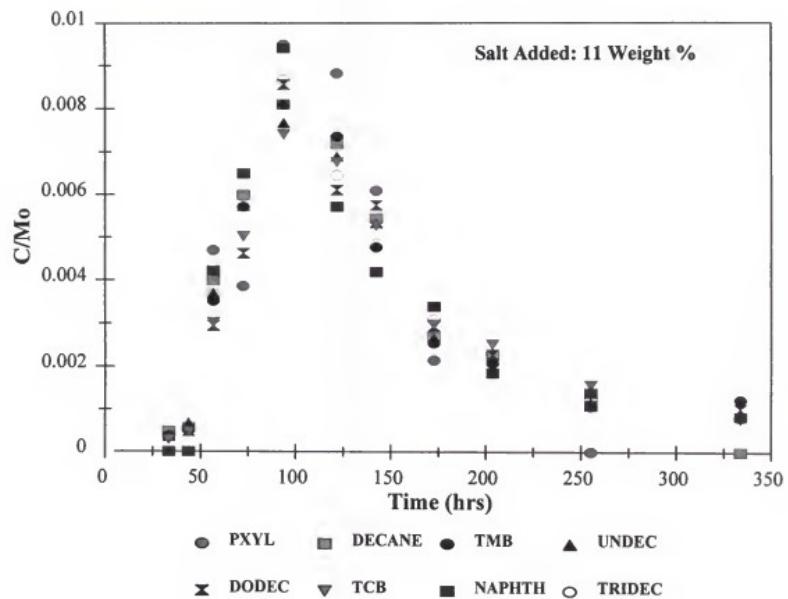


Figure 2-2 Target analytes present in the separated organic phase (11% by weight of salt added)

analytes as a function of the NAPL amount solubilized in the effluent. In Figure 2-3, volumetric separation of the SPME effluent for a fixed amount of salt is shown to mirror this consistency shown in the scaling of the concentrations to the zeroth moment. This volumetric separation was reported as the ratio of the volume of the aqueous-rich phase before separation to the total SPME effluent volume prior to separation. Therefore, not only was the composition of the organic-rich phase relatively constant for a fixed amount of salt as a function of time, but also, the volumetric phase separation that produced each of the immiscible phases remained constant.

#### Volumetric separation

Phase separation was also evaluated as a function of the amount of salt added. The amount of salt added was varied over a range of weight percentages (0%-20% by weight). Samples taken from the composite waste volume and during the elution of the 1<sup>st</sup> pore volume were separated by salt addition into organic-rich and aqueous-rich phases. Each of the separated phases were then analyzed by GC for the target analytes.

In general, the aqueous to total volumetric fractions increased as the salt added to the SPME effluent increased for both the 1<sup>st</sup> pore volume and composite volume cases (Figure 2-4). The increasing ratios depicted how the volume fraction of the aqueous phase were increasing in correspondence with the decrease organic phase volume fraction after separation. This may have been due to increased removal of water that was trapped in the organic phase either in reverse micelles or adsorbed to the surfactant by the increasing amounts of salt which tends to make the water a more polar solvent (Kabalnov et al., 1995). These results are also similar to those reported by van den Tempel (1958).

Van den Tempel found that the rate of coalescence increases rapidly with increase in

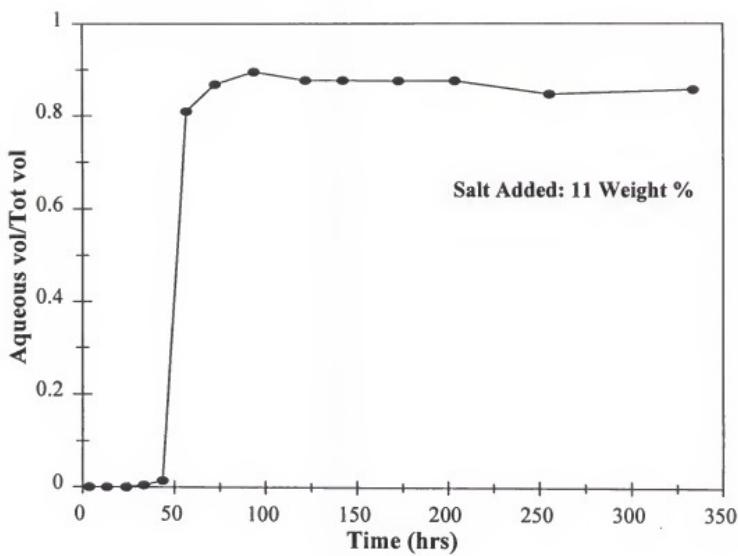


Figure 2-3 Volumetric phase separation as a function of effluent sample time (11% by weight of salt added)

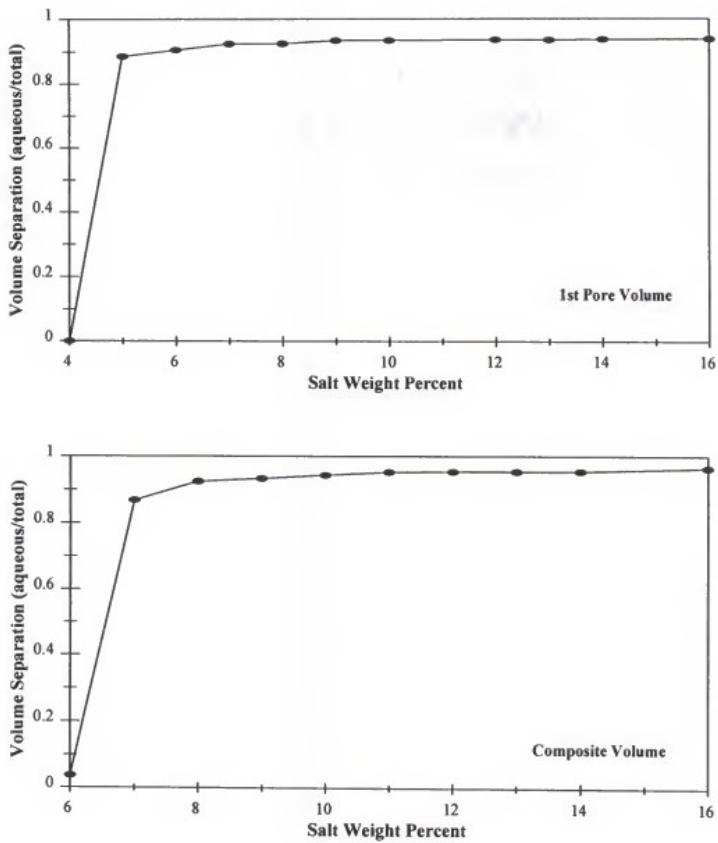


Figure 2-4 Volumetric separation of SPME effluent by addition of salt to the composite volume (top) and 1st pore volume (bottom) samples

NaCl concentration. Wasan et al. (1978) observed that increasing NaCl concentration decreased the interfacial viscosity and coalescence time, which would agree with the results shown in this paper.

Closer examination of the data showed that despite the fact that for both sets of samples the volumetric separation ratio (aqueous/total) increased with increasing salt content, they did not increase uniformly based on weight percentages of added salt. This speaks to the unpredictability of the SPME solution and this method of separation as a function of added neutral electrolyte. Although an effective method, an exact ratio can only be estimated and not predicted based on the salt added to a particular SPME system. However, it was shown that smaller amounts of NAPL in the SPME effluent resulted in a larger aqueous phase volume after separation as proven by the larger ratios seen in the composite volume compared to the 1<sup>st</sup> pore volume.

Figure 2-4 shows that both the 1<sup>st</sup> pore volume and the composite volume reach nearly equivalent values for most effective separation by salt based on the plateaus reached in the measurement of volumetric separation. At the highest salt concentrations, both sets of samples reach volumetric ratios of aqueous to total volume of approximately 0.95. Increasing salt concentration beyond these solubility limit values resulted in inefficient separation as function of salt added and was characterized by unsolubilized salt accumulating at the bottom of the separated system. It was also shown that higher amounts of salt were required by the composite volume to initially separate. But once initially separated, the composite volume quickly reached near maximum ratio (Figure 2-4, bottom). These increasing ratios demonstrated how effective the salt addition is in reducing the NAPL saturated volume that may require costly disposal methods.

### Mass partitioning

Important as it was to have significant NAPL volume reduction, another important part of the treatment process would depend upon the distribution of NAPL mass after separation. Based on GC-FID analysis of the separated phases, the mass of the target compounds, which represent the NAPL contaminant, allowed for estimation of mass partitioning percentages. Figure 2-5 displays the percentages of the mass of the target components in the separated organic-rich phase as a function of the amount of salt added to the initial SPME effluent for the composite volume and 1<sup>st</sup> pore volume samples. In both the 1<sup>st</sup> pore volume and the composite volume, extreme partitioning (usually ~ 99% mass) of the NAPL into the separated organic-rich phase was noted. This was desired because it not only allowed for a more condensed volume of NAPL saturated, organic-rich phase to be attained, but also, it may allow for the aqueous phase to be treated as merely industrial wastewater. The separated aqueous phases from the 1<sup>st</sup> pore volume and composite volume were shown to contain small portions of the target compounds which may cause industrial wastewater concerns. However, undecane was the most prevalent of these compounds and its concentration remained approximately 1 ppm, which should not be a problem for most industrial wastewater treatment facilities.

Likewise the majority of the cosurfactant, pentanol, partitioned into the organic-rich phase. Based upon mass percentages of partitioning, it was found that the amount of pentanol, unlike the target analytes, that partitioned into the organic-rich phase was a function of the amount of salt added to the system. As shown in Figure 2-6, as the amount of salt added increased, so did the percentage of the pentanol mass that partitioned into the organic phase. The reason this trend was not duplicated with the

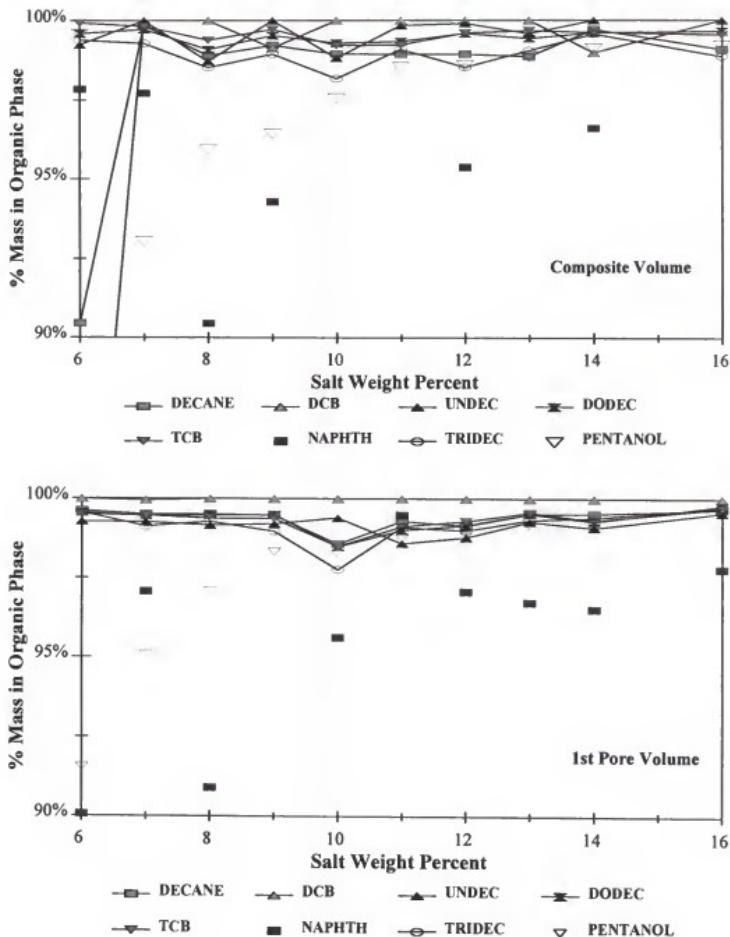


Figure 2-5 Percentages of target analyte mass partitioning into the separated organic phase as a function of the amount of salt added. Target analytes include: decane; 1,2-dichlorobenzene (DCB); undecane (UNDEC); dodecane (DODEC); 1,2,4-trichlorobenzene (TCB); naphthalene (NAPHTH); tridecane (TRIDEC); and pentanol.

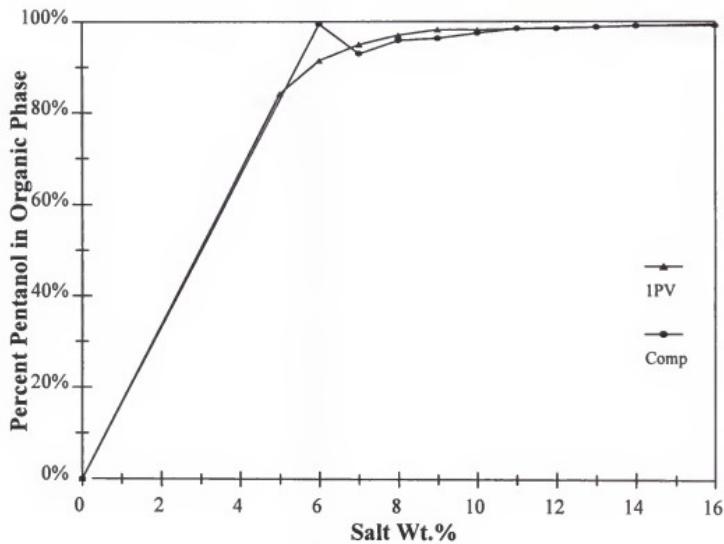


Figure 2-6 Percentages of pentanol mass partitioning into the separated organic phase of the composite volume and 1<sup>st</sup> pore volume samples as a function of the amount of salt added.

target analytes could be attributed to the nearly total partitioning of these hydrophobic components to the upper phase at even the minimal salt separation concentration.

Pentanol's increased solubility in water compared to the other components might have prevented its immediate partitioning into the organic phase at a minimal amount of salt for separation. But, as increasing salt made the aqueous phase more polar, the hydrophobic character of pentanol transported it in increasing amounts to the nonpolar organic phase.

Scaling the concentrations of the target analytes in the organic-rich phase to their initial concentrations in the SPME effluent also allowed examination of component partitioning subsequent to phase separation by salt addition. In Figure 2-7, relative concentrations in both the composite volume and 1<sup>st</sup> pore volume organic-rich phases were shown to generally increase as a function of salt added. Recalling that the mass percentages remained relatively constant as salt increased in the system, it follows that the increasing concentrations in the organic-rich phases might lead to a reduction in the volume of the organic-rich phases. This assertion was indicated by the increasing volumetric phase ratios shown earlier in Figure 2-4. These figures show that as salt addition increased, volume of aqueous-rich phase increased, which resulted in the decrease of the organic-rich phase volume. As the volume of organic-rich phase decreased in conjunction with the relatively fixed mass partitioning percentages, the target analytes in this phase should increase, as shown in Figure 2-7. Since the target analytes were present in larger concentrations in the 1<sup>st</sup> pore volume sample, as expected, its relative concentrations in the separated organic-rich phase were found to be higher than those seen in the composite volume.

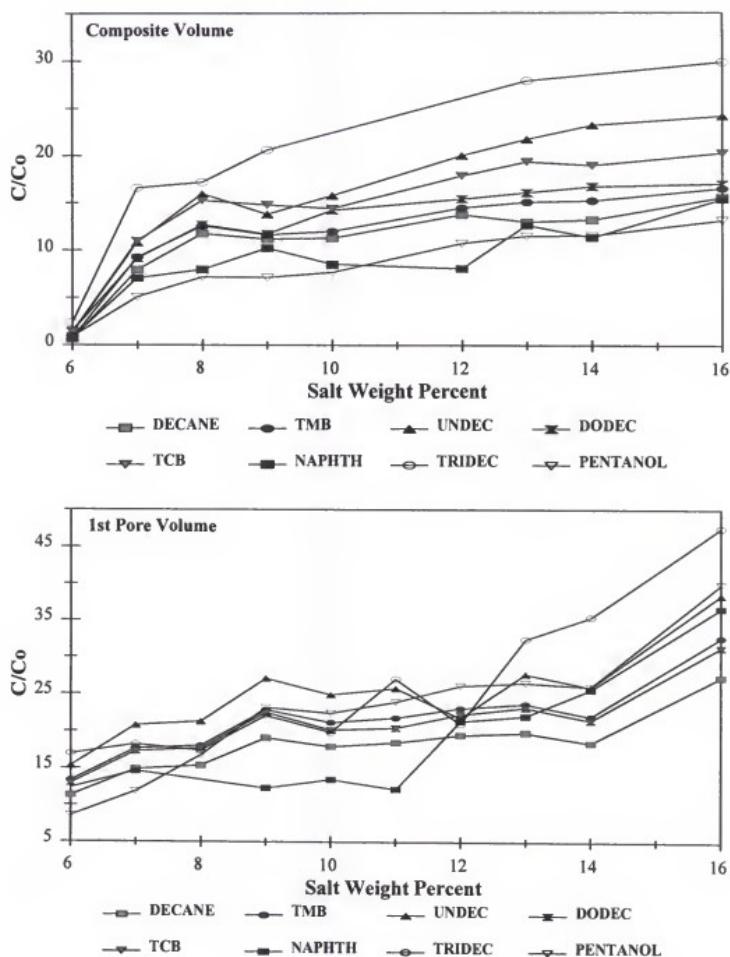


Figure 2-7 Relative concentrations ( $C/C_0$ ) of target analytes partitioning into the separated organic phase as a function of the amount of salt added. Target analytes include: decane; 1,2-dichlorobenzene (DCB); undecane (UNDEC); dodecane (DODEC); 1,2,4-trichlorobenzene (TCB); naphthalene (NAPHTH); tridecane (TRIDEC); and pentanol.

Brij 97

As listed in Rosen (1989), addition of electrolytes and change of surfactant structure decrease the solubilization capacity of the microemulsion. In the case of these experiments, the addition of salt and the resulting immiscible phases occurred in conjunction with the modification of the Brij 97 surfactant. GC-FID analysis of surfactant concentration was difficult due to its breakdown upon phase separation and the surfactant in the resulting phases no longer held a consistent analytical composition. This was made more problematic because of the variable initial composition found in different batches of Brij 97. GC analysis of several batches of the surfactant solutions revealed some variability in the intensities of several peaks. Similar problems were cited by Kibbey and Hayes (1997) in their difficulty in analyzing ethoxylated nonionic surfactants, like Brij 97, due to their multi-component composition. Consequently, in this research, quantification of the total surfactant (Brij 97) was not found to be reliable, partly because of the various C<sub>10</sub> to C<sub>40</sub> chains and especially under the situation of phase separation. However, GC chromatographic peaks belonging to Brij 97 allowed qualitative estimates of the presence of the surfactant in separated phases to be approximated. Based on chromatograms of the separated aqueous phase, a peak found in the original surfactant chromatogram was found to persist more than any other component after separation and with the least variability ( $\leq 5\%$  error). This signature peak was used to estimate, by initial concentration ratio, the amount of Brij 97 found remaining in the aqueous phase. As the surfactant concentrated in the organic phase, the Brij 97 signature peak ratio became greater than 1; while in the aqueous phase it was less than 1 as the surfactant partitioned into the hydrophobic phase. Concentrations were then calculated by multiplying these

surfactant ratios by the initial concentration of the Brij 97 in the precursor flushing solution (30,000 mg/L). Realistically, this analysis is an overestimation because it only deals with a minor component of a diverse mixture that was not uniformly separated.

Figure 2-8 displayed the relative concentration of Brij 97 found in the organic-rich phase as a function of salt. Similar to the target analytes, it was determined that increasing amounts of salt resulted in larger partitioning of the surfactant component into the hydrophobic, organic-rich phase. This behavior of the nonionic Brij 97 surfactant as a function of salt addition agreed with conclusions found in earlier literature (Kahlweit et al., 1985; 1989; Kabalnov et al., 1995). Perhaps due to the lower relative concentrations of the target analytes, more of the surfactant in the composite volume sample concentrated into the organic-rich phase compared to that of the 1<sup>st</sup> pore volume sample, however small the difference.

#### COD test

The GC analysis revealed that not only was NAPL saturated volume being decreased for further treatment or disposal, but also, that the mass of the NAPL partitioning to the organic phase was nearly complete. This may aid in the acceptability of separated aqueous phase for treatment, or allow recycling of it in the remediation process itself. The ease of treating this aqueous phase as an industrial wastewater is likely dependent upon minimizing the chemical oxygen demand (COD) concentration of this fluid.

The COD concentration in the aqueous-rich phases of the separated composite volume and 1<sup>st</sup> pore volume samples was found to decrease with increasing salt addition (Figure 2-9). This was due likely to the increased partitioning of the hydrophobic

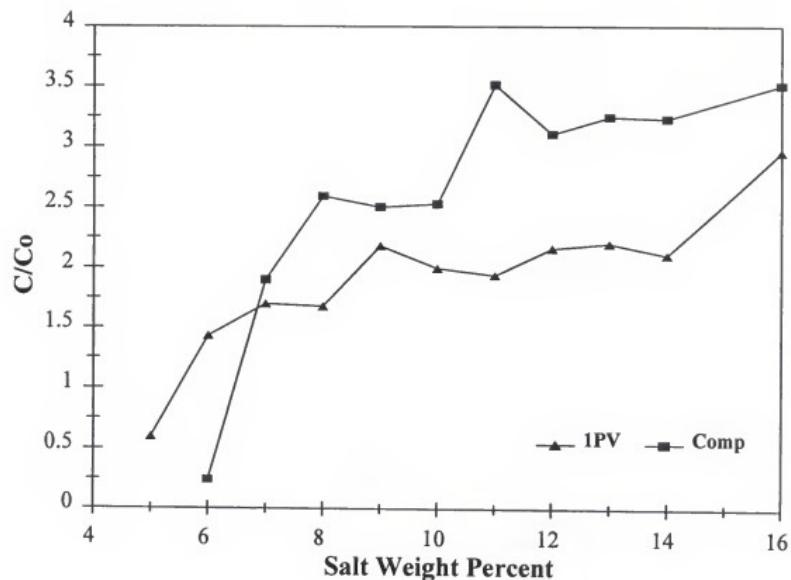


Figure 2-8 Relative concentrations of Brij 97 surfactant present in the separated organic phase in the composite volume and 1<sup>st</sup> pore volume samples as a function of the amount of salt added.

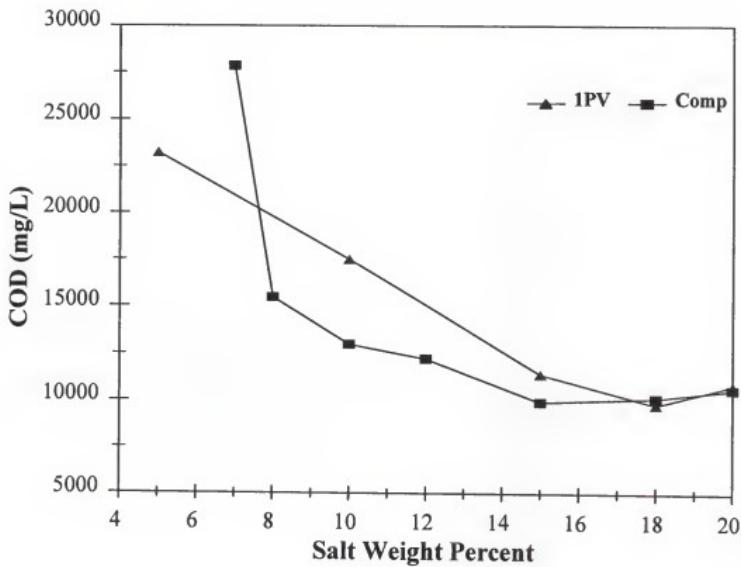


Figure 2-9 COD concentration present in the separated aqueous phase of the composite volume and 1<sup>st</sup> pore volume samples as a function of the amount of salt added

components into the organic-rich phase as salt increased. Further, it was also found that salt separation significantly reduced the COD load of the effluent by up to 1/10 concentration of the initial SPME solution. The initial COD concentration for the SPME effluent was approximately 127,000 mg/L and 120,000 mg/L for the 1<sup>st</sup> pore volume and composite volume, respectively. After the addition of ~16% of salt, the COD in the separated aqueous phase was lowered to 11,000 mg/L and below 9,900 mg/L for the 1<sup>st</sup> pore volume and composite volume, respectively.

The primary source of the COD in the industrial wastewater seems to be pentanol, based on calculations of pentanol concentration in the separated aqueous phase. Pentanol constituted up 99% of the total COD load of the separated organic phase, and approximately 100% in the aqueous phase. This direct relationship between the COD concentration and pentanol was displayed in samples taken over the duration of the SPME flush (Figure 2-10); and as a function of salt phase separation (Figures 2-11). Therefore, a majority of the COD load could be reduced by removal of pentanol by either air sparging or other inexpensive treatment technologies, thereby, increasing the cost efficiency of aqueous-rich treatment by an industrial wastewater facility.

#### Field Test

At the Hill AFB field site, NaCl was added to the SPME effluent to study its effectiveness in separating the waste into immiscible phases in the field. The tests were conducted in a glass 25 L (6.5 gallon) container and a 208 L (55 gallon) steel drum. The sample containers were filled with a composite of the effluent flushed from the subsurface isolated cell mentioned previously Rao et al. (1997). From preliminary laboratory experimentation, it was determined that for the proposed

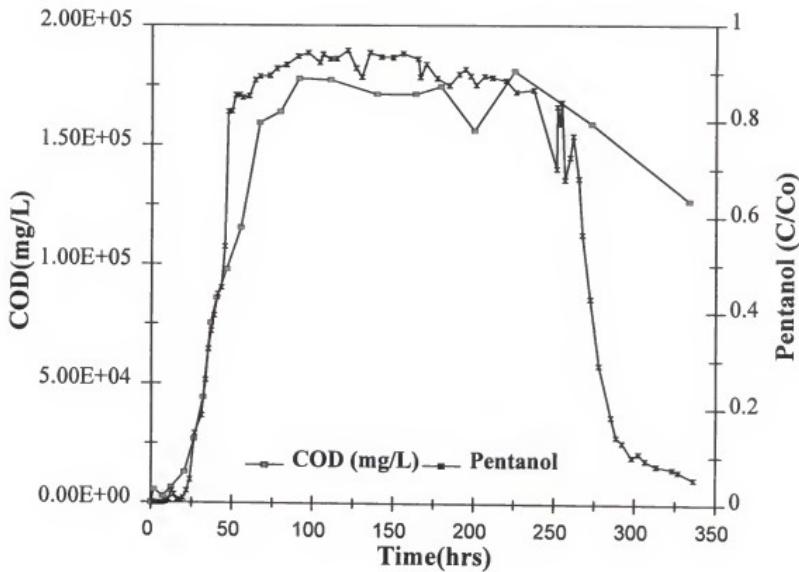


Figure 2-10 Comparison between the relative concentration of pentanol and the COD concentration over the length of the SPME flushing experiment

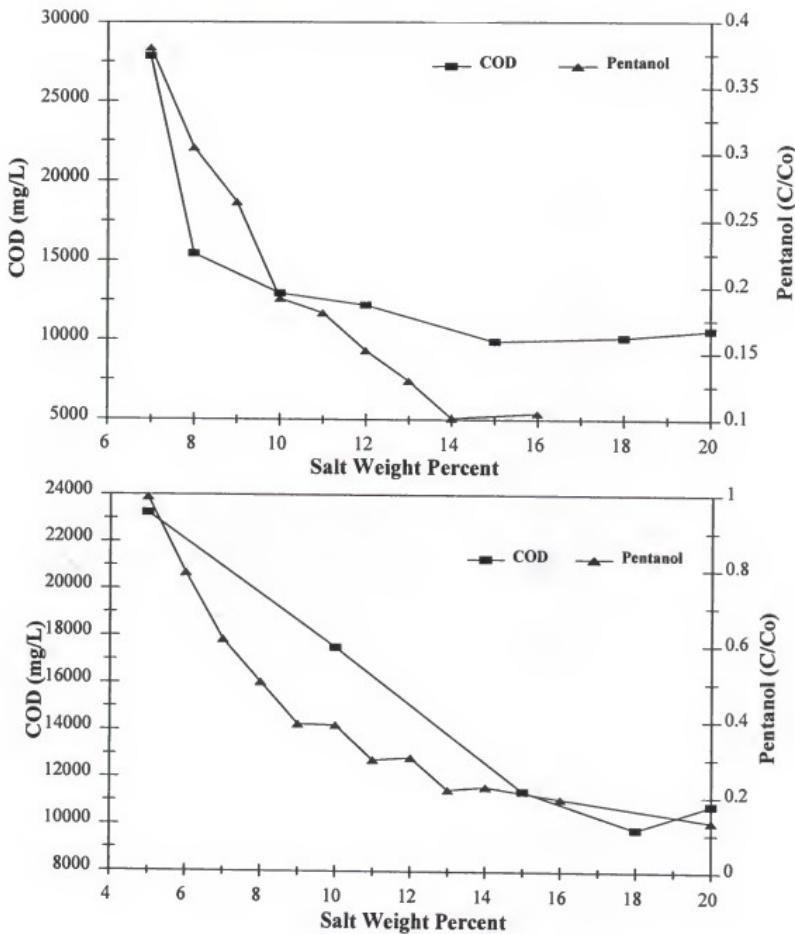


Figure 2-11 Comparison between the relative concentration of pentanol and the COD concentration in the separated aqueous phase as a function of the amount of salt added to the composite volume sample (top) and the 1<sup>st</sup> pore volume sample (bottom)

surfactant/cosurfactant mixture (3.0% Brij 97/ 2.5% pentanol) the addition of approximately 11% by weight of NaCl would provide adequate phase separation. Temperature at the field site was determined to be ~ 29°C. The NAPL was a complex mixture of jet fuel and solvents which was characterized by Rhue et al. (1997) for the following constituents (mass fraction, g/100g of NAPL): p-xylene, 0.144; 1,2,4-trimethylbenzene, 0.438; n-decane, 0.477; n-undecane, 1.573; n-dodecane, 0.698; and n-tridecane, 0.285).

Comparing data gathered at the field site and in the laboratory with the same experimental parameters indicated that there was relatively little difference between the results gathered in the laboratory and in the field (Figure 2-12). The lower field concentrations were attributed to the difficulty in measuring low concentrations, and possible volatilization losses during sample collection and transport.. Based on concentrations of the target compounds and pentanol found in the separated organic and aqueous phases in both the field and laboratory experiments, it can be assumed that the separations conducted in the laboratory would be fairly representative of what might occur in the field.

In the 25 L glass bottle, the separation occurring over time was documented by photos taken at the field site (Figure 2-13). Samples were taken from three different levels in the glass carboy, these included: the top separated organic layer, the bottom of the separated aqueous phase, and from the middle of the separated aqueous phase. Each of these levels in the separated layers were analyzed by GC-FID to determine their composition concerning the previously mentioned target compounds and pentanol (Table 2-1). Similar to the laboratory experiments, it was shown that the majority of the target

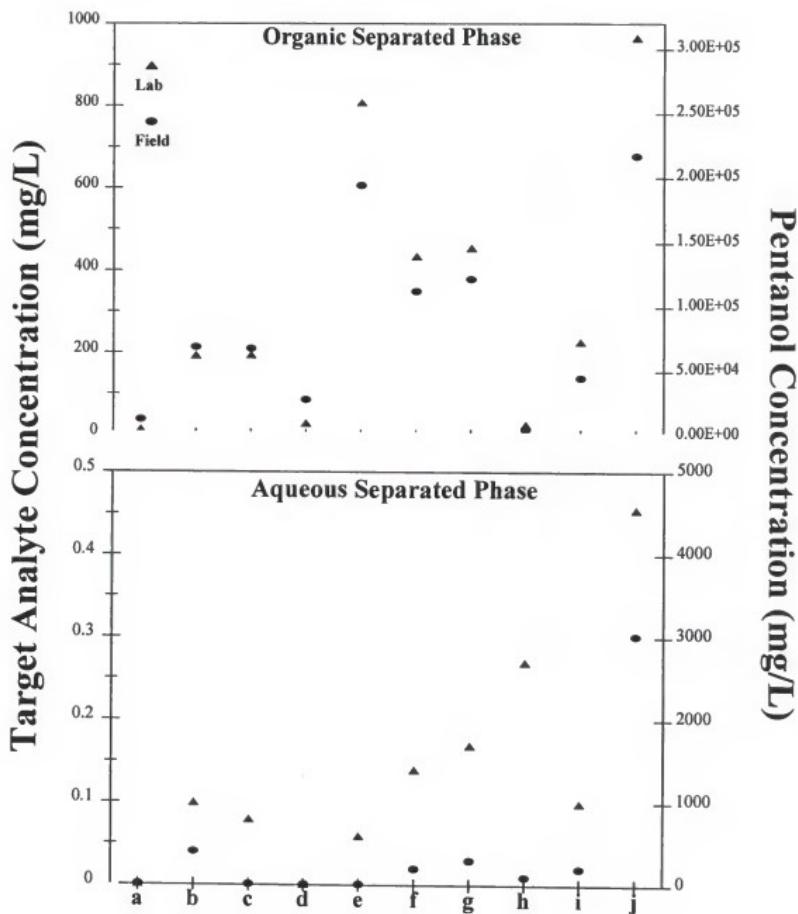


Figure 2-12 Comparison of field data and laboratory data for SPME separation at 11 weight percent of salt added. Target compounds include a :p-xylene; b :decane; c :trimethylbenzene; d :dichlorobenzene; e :undecane; f :dodecane; g :trichlorobenzene; h :naphthalene; i :tridecane; j :pentanol.



Initial SPME  
effluent

After addition  
of 11 wt.% NaCl

Two hours after  
NaCl addition

Six hours after  
NaCl addition

Figure 2-13 Field separation of SPME effluent at Hill AFB, Utah (11 weight percent of salt added)

Table 2-1. Field Results of Intermediate Treatment of SPME by Salt Addition at 11 weight percent. Concentration of components listed in mg/L separated phase.

Target Compounds	P-xylene	Decane	1,2,4-Trimethyl benzene	Undecane	Dodecane	1,2,4-Trichloro benzene	Tridecane	Pentanol	Brij 97 Surfactant
<b>25 L glass carboy</b>									
Top(org)	37.80	213.80	210.10	606.40	351.60	381.50	140.50	2.17*10 <sup>5</sup>	4.77*10 <sup>4</sup>
Middle (aq)	----	0.48	----	0.04	0.16	0.19	0.08	6.87*10 <sup>3</sup>	8.64*10 <sup>3</sup>
Bottom (aq)	----	0.04	----	----	0.02	0.03	0.02	3.02*10 <sup>3</sup>	231
<b>208 L drum (3 feet tall)</b>									
Top (org)	23.40	138.90	154.30	462.70	343.00	328.00	178.30	9.36*10 <sup>4</sup>	4.61*10 <sup>4</sup>
1 ft from surface (aq)*	2.84	13.74	14.86	41.58	26.91	24.70	12.10	9.82*10 <sup>3</sup>	3.75*10 <sup>4</sup>
2 ft from surface (aq)*	2.00	10.09	10.30	24.42	19.20	18.01	6.68	8.73*10 <sup>3</sup>	2.70*10 <sup>4</sup>
Bottom (aq)	----	0.28	----	----	0.06	0.09	0.04	2.63*10 <sup>3</sup>	609
SPME (prior to separation)	1.28	11.52	11.20	35.70	23.63	21.07	7.26	2.52*10 <sup>4</sup>	3.00*10 <sup>4</sup>

----: Below detectable limits

aq : Aqueous-rich phase

org: Organic-rich phase

\*: Incomplete separation

compounds partitioned into the separated organic-rich phase, while only a small remnant of these compounds remained in the aqueous phase. The separated volumes were not individually quantified, so the partitioning of the target compounds into both phases was based on concentrations of the components via GC-FID analysis.

The targeted long-chain aliphatic compounds (undecane, dodecane, and tridecane), which are known to make up the majority of fuels-grade contaminants, were significantly removed to the upper organic layer away from the aqueous phase. The middle areas were found to contain a relatively higher concentration of the target compounds than the bottom of the containers, however, they still contained significantly less components than the upper organic phase. Table 2-1 shows that for the target analytes and pentanol, the highest ratio of a component in the upper phase to the lower and middle phases occurs with decane. However, even in this case, the upper phase contained a much larger concentration (213.8 mg/L) than the middle (0.48 mg/L) and lower phase (0.04 mg/L). The other target compounds were present at even lower amounts in the bottom and middle portions of the carboy than the ones found for decane, which demonstrate the effective removal of the NAPL to the upper organic phase.

#### Pentanol

The increase in concentration of target compounds in the middle portion of the carboy can be attributed to the incomplete partitioning of the surfactant and cosurfactant between the two immiscible phases. It was shown in Table 2-1 that a majority of the pentanol partitioned into the upper separated organic phase, but not as well as the target compounds. The reluctance of pentanol to leave the aqueous phase can be attributed to its high solubility in water. The high salt presence in the bottom level of the carboy, in

conjunction with pentanol's affinity for hydrophobic components as well, caused the pentanol be drawn away from the bottom level into upper and middle levels in the system. Despite the fact that most of the pentanol partitioned into the separated organic phase (217,000 mg/L), pentanol's high solubility in water prevented the almost total partitioning into the upper organic phase seen in the case of the target analytes, and a significant portion was found in the middle level of the system. This middle level contained twice the amount of pentanol (6870 mg/L) than that found in the very bottom level of the aqueous phase (3020 mg/L), but was still substantially less than the amount that partitioned to the upper level.

#### Brij 97

As shown on Table 2-1, estimated concentrations of the Brij 97 signature peak indicate that although a majority of the surfactant components partitioned into the organic phase, some remained in the aqueous phase after separation by salt. This residual amount of the surfactant in the separated aqueous phase was most likely part of the hydrophilic portion of the surfactant composition, and was presumably responsible for there not being a total partitioning of hydrophobic components into the upper organic phase.

#### Scale up

A separation experiment was also conducted in a 208 L drum on site to determine how the process efficiency would react under slight scale up conditions. Judging by the data on Table 2-1, it was determined that poor separation occurred in this system, especially in examination of the intermediate levels of the drum. This incomplete separation can be blamed on inefficient mixing and lack of visual confirmation of separation after mixing was stopped. Aside from the poor level of separation in the

intermediate levels, the top level did acquire a majority of the target compounds and the bottom level was almost devoid of these compounds after separation. Separation in the 208 L drum did occur at some level, however, with more efficient mixing procedures for larger volumes such as siphon pumps or the like, better separation in the intermediate levels might also be achieved as observed in the 25 L glass carboy.

### Cost Analysis

The utility of this intermediate waste treatment process is based on economic advantages. Using the results gathered from the laboratory experiments and cost estimates from the field work, a cost analysis of the intermediate treatment of the SPME effluent with salt as a function of the amount of salt added was conducted. This analysis was executed to show the effect of the intermediate treatment of salt addition on the cost of the remediation process.

Cost assumptions included factoring in the cost of remediation of the SPME effluent by incineration, cost of treating the aqueous and organic separated phases, and the cost of the salt. Since the process is relatively spontaneous and only requires moderate mixing, power inputs were assumed negligible. Incineration of the SPME effluent itself was estimated at \$1.73/gallon based on Hill AFB cost quotes by CH2M Hill (CH2M Hill, 1997). The phase separation resulted in an aqueous phase that could be treated by an industrial wastewater treatment process at a cost of \$2/1000 gallons. The organic phase produced by phase separation was assumed to be incinerated as a fuel grade fluid (<20% water) at a cost of \$0.115/lb. The cost of salt at \$0.21/lb for a 100 lb bag was referenced from Apperson Chemical Inc., in Jacksonville, Florida. However, for large bulk order, the cost of salt may found to reduce per pound.

Basing the analysis on the estimated 20,000 gallons of SPME effluent, the cost of treating the non-separated effluent was calculated to be approximately \$34,600. The effect of incorporating the intermediate salt addition treatment process (Figure 2-14) decreased the cost of treatment to just above \$4,000 for the same 20,000 gallons of SPME effluent. The volume and cost of NAPL to be incinerated decreases with the increase in salt addition and the increase in the amount of aqueous phase volume for treatment. Both the composite volume and 1<sup>st</sup> pore volume samples reach a minimum cost for an effective amount of salt used for separation. In both instances, the more salt was shown to not necessarily be more effective. Treatment of different microemulsion mixtures would probably deviate from these cost results due to differences in composition and separation properties.

### Conclusions

The purpose for this experiment was to explore a phase separation procedure to reduce the amount of waste that would require expensive treatment by incineration. The waste was an effluent single phase microemulsion (SPME) from subsurface flushing of a contaminated soil. Addition of a neutral electrolyte (NaCl) to the SPME was found to produce significant phase separation of the microemulsion. It was determined that salt effectively separated the SPME effluent into two immiscible phases for further treatment and/or disposal. This intermediate treatment method was found to be effective and relatively constant for both in field and laboratory applications.

Data provided evidence that there was no preferential partitioning of the different compounds over the length of the flushing experiment. Phase separation by salt addition

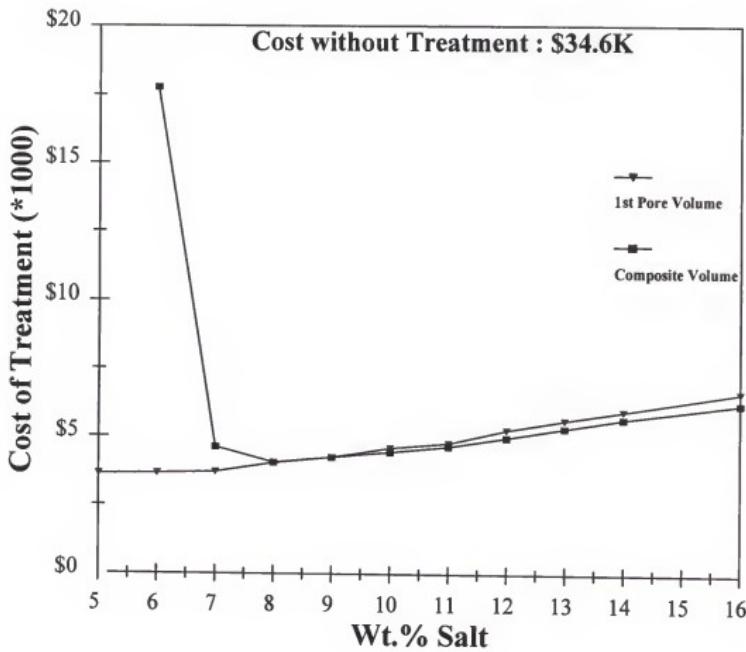


Figure 2-14 Cost analysis of intermediate waste treatment procedure in which salt addition to the SPME effluent is incorporated

was also found not to promote preferential partitioning of components into the organic-rich phase. The composition of the organic-rich phase was relatively constant for a fixed amount of salt as a function of time, and for the volumetric phase separation that produced each of the immiscible phases.

The ratio of aqueous phase volume to total volume fraction increased with increasing addition of salt. Additionally, both the 1<sup>st</sup> pore volume and the composite volume samples reach nearly equivalent plateau values for most effective separation by salt based on measurement of volumetric separation. At the highest salt concentrations, both sets of samples reach volumetric ratios of approximately 0.95 for aqueous volume to total volume measurements.

Based on percentages of the target component mass found in the separated organic-rich phase, almost total partitioning (usually ~ 99% mass) of the NAPL into the separated organic-rich phase was observed for both the 1<sup>st</sup> pore volume and the composite volume samples. Conversely, the pentanol that partitioned into the organic-rich phase increased as a function of increasing salt presence in the system. Scaled relative concentrations for the target analytes and surfactant found in the separated organic-rich phase were observed to increase as salt addition increased for both composite volume and 1<sup>st</sup> pore volume samples.

The COD concentration in the aqueous-rich phase was found to decrease with increasing salt addition. It was also found that salt separation significantly reduced the COD load of the effluent by up to 1/10 concentration of the initial SPME solution.

A cost analysis suggested that neither the higher or lower the amount of salt added was the most cost efficient method of intermediate treatment. Additional factors based on

treatment of the separated phases aid in determining the most practical amount of salt required for treatment. The use of NaCl was found to reduce the amount of waste that would require treatment by expensive incineration. The money saved by using this intermediate treatment process could aid in the conservation of resources required by remedial flushing, as well as contributing to the overall attractiveness of employing such a process at a contaminated field site.

## CHAPTER 3

### WASTE MANAGEMENT OF A MICROEMULSION USING ELEVATED TEMPERATURES

#### Introduction

Residual non-aqueous phase liquid (NAPL) contamination has been shown to be effectively removed from the subsurface by the addition of chemicals to water which is then flushed through the zone of contamination (Sabatini et al., 1996; Chevalier et al., 1997; Rao et al., 1997). A recent study by Jawitz et al. (1998) described the use of a surfactant/cosurfactant mixture in the remediation of a hydraulically isolated test cell at Hill AFB, Utah. In that study, it was shown that approximately 95% of the most prevalent NAPL contaminants were removed by the single phase microemulsion (SPME) flood that was conducted at the site. Concern then shifted to managing the resultant waste from the remediation process. Destructive measures, such as incineration, are most often used to treat the resultant hazardous waste. However, incineration has been shown to be an expensive process (Perdek, 1997). This research focuses on the reduction of the amount of NAPL saturated liquid that would require expensive treatment by incineration. Phase separation can be used to produce a hydrophobic, organic-rich layer and a hydrophilic, aqueous-rich layer from the single SPME mixture. This reduction of the NAPL saturated volume by phase separation can be achieved by change of the ambient

temperature of the SPME solution. Increase of the temperature of a nonionic microemulsion mixture has been shown to cause phase separation resulting in surfactant partitioning into upper organic phase layer (Kahlweit et al., 1989; Rosen, 1989). The presence of both surfactant and hydrophobic NAPL contaminants in the organic phase layer results in a bottom aqueous-rich phase that can be handled by relatively inexpensive industrial wastewater treatment methods.

The objectives of this research were: 1) to investigate separation efficiency of the field generated SPME effluent over a range of temperatures; 2) to investigate the partitioning of the NAPL and surfactant into the separated organic and aqueous phases as a function of temperature; and 3) to evaluate the chemical oxygen demand of the aqueous-rich phase as a function of temperature.

### Background

Presently, there is literature which deals with the phase equilibrium of surfactant systems as a function of temperature. Most of the research in this area is relatively recent and should increase with increasing use of surfactants. Generally, an increase in temperature results in destabilization of microemulsions (Menon and Wasan, 1985; Rosen, 1989; Kahlweit et al., 1990). Menon and Wasan (1985) offered that increasing temperature increases the rate of adsorption, the van der Waals forces, and Brownian motion, and decreases the viscosity of the continuous phase film. Increase in temperature also leads to a decrease in bulk phase viscosity. This decreased viscosity of the bulk phase film increases the probability of rupture of micelles, and then, coalescence of the

immiscible organic phase. Alexandridis et al. (1995) described the coalescence in a phase system due to increasing temperature as a function of the increasing effective diameter of the droplets. This increase in droplet diameter leads to the increased frequency of droplet collisions and an increased droplet coalescence rate. Alexandridis et al. (1995) said that this increase in droplet diameter and the exchange of material after coalescence facilitates cluster formation and expedites phase separation.

Wade et al. (1978) showed that in a ionic surfactant/cosurfactant mixture, the increase in temperature resulted in a decrease in interfacial tensions in the system. This decrease in interfacial tension would favor micellization and more oil may be solubilized into a single-phase system. However, Kahlweit et al. (1989, 1990) and Lake (1989) have shown that the nonionic surfactant systems display inverse behavior to that of ionic systems, especially in temperature and other cases influencing phase stability such as oil carbon number and salt concentration. This leads to the concept that as temperature in a nonionic system increases, interfacial tension also increases which inhibits micellization and results in the phase separation of a single-phase system.

Kahlweit et al. (1990) stated that at ambient temperatures nonionic surfactants are more soluble in the aqueous phase, which denotes a Winsor I system like that seen in the SPME flushing precursor solution used at Hill AFB (Jawitz et al., 1998). However, at elevated temperatures, Kahlweit et al. (1990) indicated that the nonionic surfactants are more soluble in the upper oil-rich phase (Figure 3-1, top). Kahlweit et al. (1990) continued by showing the contrasting effects of temperature on nonionic and ionic surfactants as functions of hydrophobicity of the amphiphile and salt concentration.

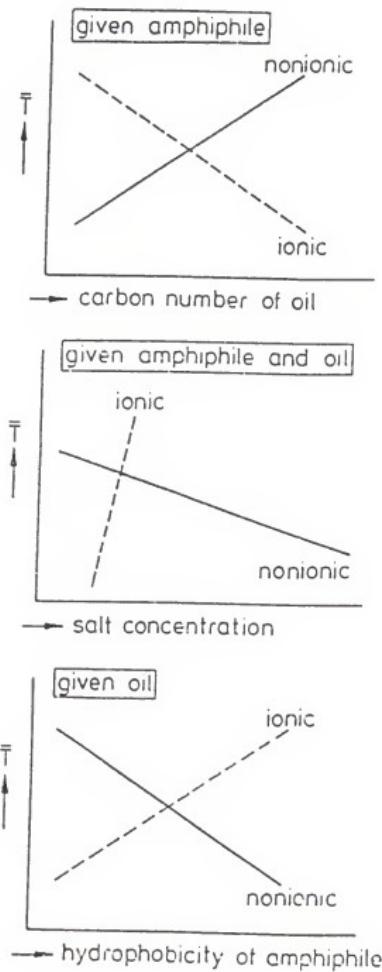


Figure 3-1 Temperature effects on the behavior of nonionic and ionic surfactants dependent on the given surfactant (amphiphile) and oil as functions of carbon number of oil (top), salt concentration (middle), and hydrophobicity of surfactant (bottom).

Kahlweit (1995) later showed the different effects of temperature on nonionic and ionic surfactants partitioning into immiscible phases (Figure 3-2). In Figure 3-2, it is shown that for nonionic surfactants, as temperature increases, that the surfactant would partition more into the separated organic-rich phase ( $\bar{2}$ ) and not to the aqueous-rich phase ( $\underline{2}$ ).

Ionic surfactants are shown to behave differently than nonionic surfactants as a function of temperature and surfactant distribution coefficient ( $K_C$ ).  $K_C$  was noted as the distribution coefficient of surfactant between the oil (o) and aqueous (a) phases.

As shown by Kahlweit et al. (1990) and Kahlweit (1995), temperature plays a dominant role in the formulation of nonionic microemulsions along with the nature of the hydrocarbon. The hydrophile-lipophile balance (HLB) number, which is unitless, is an indicator of the relative strength of the hydrophilic and hydrophobic portions of the surfactant molecule, and can be used to characterize the relative affinity of surfactants to either aqueous or organic phases. A high HLB usually indicates good solubility of a surfactant in water, while a low HLB depicts a surfactant which better solubilizes in the organic phase. Brij 97 was listed as having a relatively high HLB of 12.4 (Rhue et al., 1997), which denotes a very water soluble surfactant. However, Rosen (1989) stated that an increase in temperature causes the degree of hydration of a polyoxyethylenated (POE) nonionic surfactant to decrease, which makes the surfactant less hydrophilic. Therefore, the HLB of the nonionic surfactant must decrease and the surfactant is more likely to partition into the separated organic-rich phase. Regardless of how water-soluble a nonionic surfactant may be, increasing temperature reduces its aqueous phase solubility.

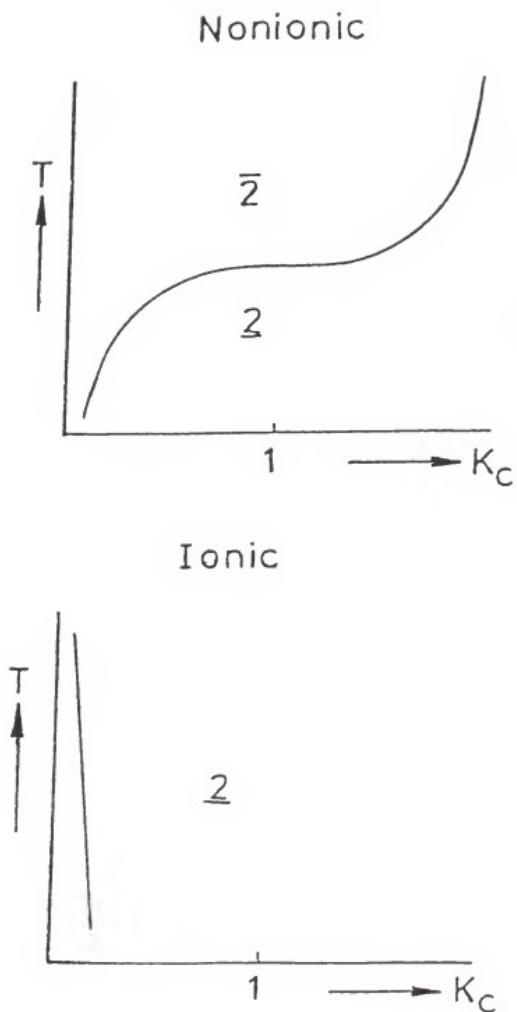


Figure 3-2 Temperature dependence of the distribution of nonionic (top) and ionic (bottom) surfactants between oil and water mixtures. (Kahlweit, 1995).

and leads to surfactant partitioning into a more hydrophobic separated phase. This assertion is indicative of the fact that microemulsions with nonionic surfactants are extremely temperature sensitive (Friberg and Venable, 1983).

The temperature at which clouding and then phase separation occurs depends on the structure of the polyoxyethylenated nonionic surfactant. For a particular hydrophobic group, the larger the percentage of oxyethylene in the surfactant molecule, the higher the cloud point, although the relation between oxyethylene percentage and cloud point is not linear. For nonionic polyoxyethylenated surfactants, like Brij 97, the effect of temperature increase appears to depend on the nature of the solubilizate. Nonpolar compounds, such as aliphatic hydrocarbons and alkyl halides, which are solubilized in the inner core of the micelle, appear to show increased solubility as the temperature is raised, the increase becoming very rapid as the cloud point of the surfactant is approached (Saito, 1967; Saito and Shinoda, 1967). Rosen (1989) stated that this rapid increase just below the cloud point probably reflects the large increase in aggregation number of the micelles in this region and the transition from spherical to more asymmetric micelles.

The increase in the aggregation number of the micelles occurs soon after CMC (critical micelle concentration) has been reached in the system. The CMC of surfactants, like the aggregation number, is temperature dependent. Lake (1989) stated that the effect of temperature on the CMC surfactants in aqueous medium is complex, the value appearing first to decrease with temperature to some minimum and then to increase with further increase in temperature. Temperature increase causes decreased hydration of the hydrophilic group, which favors micellization. However, temperature increase also

causes disruption of the structured water surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range. As the CMC increases, the formation of micelles is less likely and the single-phase microemulsion cannot form. So, by increased temperatures disfavoring the micellization in a nonionic system, the system is forced out of the single-phase region. Crook et al. (1963) stated that the minimum in the temperature-CMC curve appears to be around 50°C for nonionic surfactants, while for ionics this minimum is around 25°C according to Flockhart (1961). This was taken into account for the Brij 97 surfactant used in this research based on personal communication from ICI Surfactants (Gary Holliday: 4/29/97 to Pat Aikens) which stated that Brij 97 has a cloud point around 70°C and phase inversion temperature (PIT) of 50°C without cosurfactant.

Rosen (1989) also stated that nonionic surfactants are subject to coacervation at increased temperatures, which refers to the formation of a separate surfactant-rich phase at the cloud point. Kahlweit et al. (1990) added that the critical temperatures at which phase transitions occur depend not only on the surfactant, but the oil component as well. Kahlweit et al. (1990) concluded that the temperature for phase transitions rises with increasing carbon number of the oil but drops with increasing carbon number of the tail of the surfactant, for a given surfactant and oil, respectively. However, the addition of medium or long chain alcohols, such as pentanol, to surfactant produced microemulsions has been shown to cause temperatures of phase separation to decrease (Kahlweit et al., 1991). These factors would therefore directly affect the production of immiscible phases.

Increasing temperature basically makes water a worse solvent for polyethylene oxide, therefore, the surfactant polar heads contract, and the monolayer changes its spontaneous curvature which may cause a bend towards water. Generally, a more polar hydrocarbon as an oil component produces a shift in the three-phase body to lower temperatures (Kabalnov et al., 1995).

#### Materials and Methods

Liquid samples were taken periodically from the effluent of the combined extraction wells from the surfactant flushing of the subsurface test cell 8 in OU1 at Hill Air Force Base, Utah. A circulating water bath, set at various temperatures, was used to separate the effluent SPME into immiscible phases. Samples taken over the length of the flushing experiment were immersed in the bath for a minimum of 15 minutes up to a maximum of 30 minutes.

Both the upper organic phase and the lower aqueous phase were collected after separation. The upper separated organic layer was diluted (1:10) in methylene chloride ( $\text{MeCl}_2$ ). The  $\text{MeCl}_2$  solution and the aqueous phase were both analyzed by GC-FID for target analytes and for the cosurfactant, pentanol. This extraction of the upper layer was important to determine how efficient the separation of the NAPL and the pentanol from the effluent microemulsion dependent upon temperature. For extraction procedure, the 1:10 ratio of  $\text{MeCl}_2$  was batch extracted on a rotary shaker for 2 days for equilibrium to be reached.

A Perkin-Elmer Gas Chromatograph with a DB-624 Column was used to analyze the microemulsion and the MeCl<sub>2</sub> extract of the separated oil phases for pentanol and target analytes. These target analytes include: p-xylene, dichlorobenzene, 1,2,4-trichlorobenzene, decane, undecane, dodecane, 1,2,4-trimethylbenzene, and tridecane.

Chemical oxygen demand (COD) tests were conducted based on the EPA approved (Federal Register, 1980) Reactor Digestion Method 8000 found in DR/2000 HACH Spectrophotometer Handbook with HACH High Range Plus COD Reagent (Loveland, CO). The high level wastes were also analyzed with colorimetric determination with a Milton Roy Spectronic 21D Spectrophotometer.

### Results and Discussion

The purpose for this study was to determine the effectiveness of phase separation of a single-phase microemulsion waste by increasing the ambient temperature of the system. Separate minor tests were conducted to ensure that the SPME effluent samples in the sample vials were exposed to the temperatures that were being read from the circulating bath thermometer. Testing showed that after a minimum of 15 minutes the temperature of the fluids inside the sample vials were found to be within 1 °C of the bath temperature. Therefore, it was assumed that temperatures in the effluent sample vials were virtually equivalent to those read by the circulating water bath thermometer.

Earlier, Figure 2-1 showed that the composition of the SPME based on the target analytes, was relatively constant over the length of the flushing experiment. Similarly, scaling concentration of target analytes in the separated organic phase to the zeroth

moment (C/Mo) showed that separation of SPME samples at a temperature of 70°C over the duration of the flushing experiment was relatively homogeneous in composition (Figure 3-3). Although the component amount in the organic-rich phase may have changed over time, the separation of the components into the organic-rich phase was relatively constant over time. Figure 3-4 verifies this assertion by displaying that the volumetric phase separation at a constant temperature of 70°C was generally constant over the length of the flushing experiment. Therefore, the relative component concentrations and overall volumetric phase separation agree when evaluating constant temperature separation as a function of time.

#### Volumetric Separation

As previously stated in Chapter 2, the volumetric phase separation was evaluated on the basis of taking the ratio of the volume of the remaining aqueous-rich phase after phase separation to the volume of the SPME waste prior to phase separation. In general, for both composite volume and 1<sup>st</sup> pore volume samples, it was shown that as temperature increased, the aqueous-rich volumetric fraction of the separated SPME increased as well (Figure 3-5). Shown in Figure 3-5, the composite sample initially broke just below 60°C, while the 1<sup>st</sup> pore volume sample did not separate until ~70°C. This difference in separation temperatures can be attributed to the different composition of the samples. NAPL constituents were present in smaller concentrations in the composite volume sample. The concentration of the oil based on NAPL constituents in the 1<sup>st</sup> pore volume was about 5200 mg/L, while in the composite sample it was just over 2200 mg/L. Additionally, pentanol had a concentration of 17,400 mg/L and 25,200 mg/L for the 1<sup>st</sup>

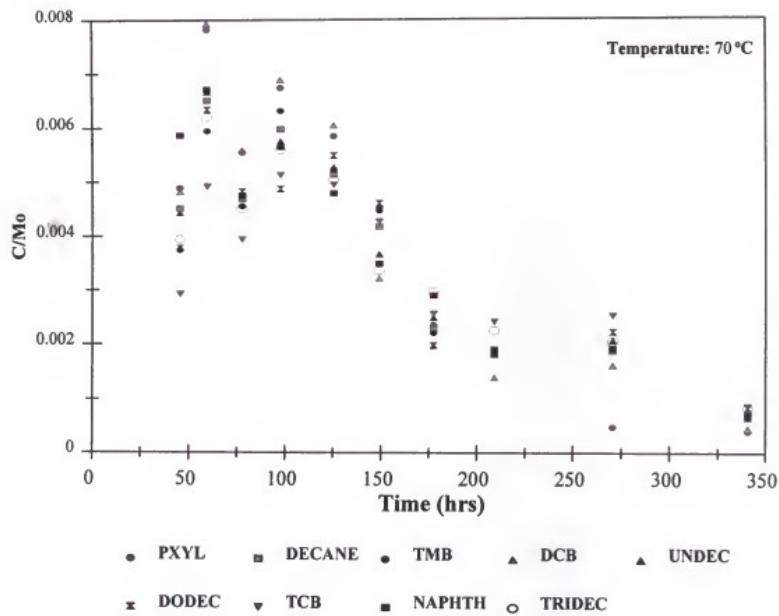


Figure 3-3 Target analytes present in the separated organic phase (11% by weight of salt added)

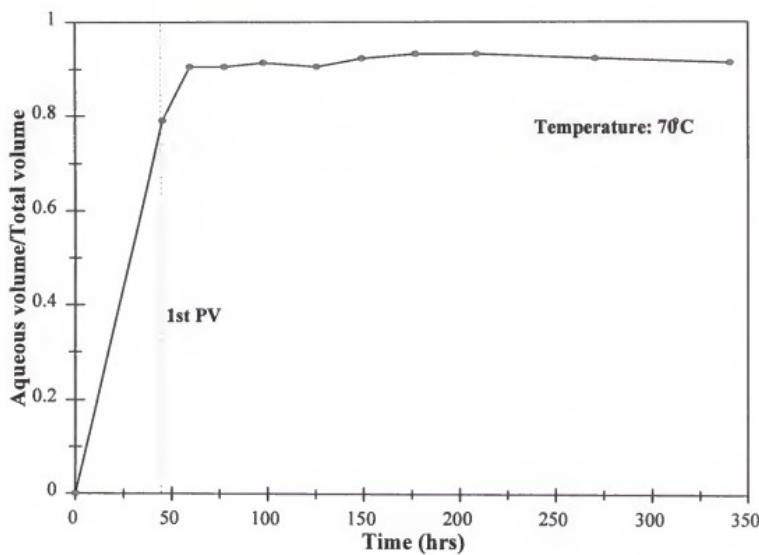


Figure 3-4 Volumetric phase separation as a function of effluent sample time  
(70°C ambient temperature)

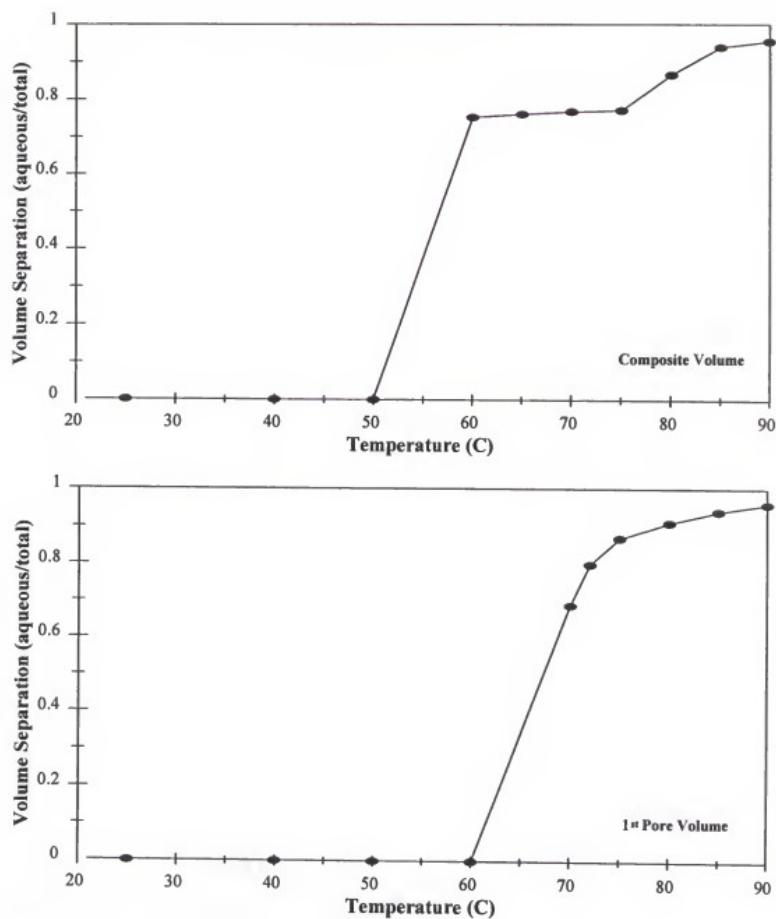


Figure 3-5 Volumetric separation of SPME effluent by increasing the ambient temperature of the Composite volume (top) and 1st Pore volume (bottom) samples

pore volume and composite volume, respectively. These values indicate a decrease in the NAPL concentration, and an increase in the pentanol concentration as the flushing experiment continued. So, the difference in separation temperatures may have occurred because the hydroxide in the pentanol is attracted to the water molecules in the bulk SPME solution due to hydrogen bonding (Snoeyink and Jenkins, 1980) and this attraction between the ionic groups in the SPME mixture leads to separation of the ionic and nonionic components in the micelles. Thus, easier separation of the composite volume sample was due to the higher concentration of polar groups present in the system, which made it increasingly difficult for both ionic and nonionic constituents to remain together in a stable, single-phase microemulsion (Rosen, 1989; Kabalnov et al., 1995).

Increasing the temperature served to increase phase separation efficiency until an optimum separation was achieved. This optimum separation for both sets of samples occurred approximately at a volumetric separation fraction of 0.96 (ratio of aqueous volume to total SPME volume). Beyond a temperature of 90 °C, the level of volumetric separation of the SPME does not improve. Although the earlier (at a lower temperature) separation of the composite sample compared to the 1<sup>st</sup> pore volume sample was attributed to the difference in their respective compositions, the optimum separation ratio seen above 90 °C was due to their basic similarity in composition. As stated in the literature (Rosen, 1989), the nonionic Brij 97 surfactant partitioned more into the organic-rich phase as temperature increased; and when it had been removed from the aqueous phase, volumetric separation of the immiscible could no longer improve. This point was reached apparently around 90 °C.

### Mass Partitioning

After initial separation at a temperature of 55°C, the mass percentages of the NAPL target components partitioning into the organic-rich phase of the composite volume sample seemed to decrease for about 10 degrees, then steadily began to rise (Figure 3-6, top). Mass percentages continued to rise to maximum values around 75°C, and then decreased again. These percentages indicated, however, that relatively complete mass partitioning of the target components into the organic-rich phase with values generally greater than 80%. For the 1<sup>st</sup> pore volume, after initial separation at 70°C, mass percentages of the targeted NAPL analytes partitioning into the organic-rich phase decreased as temperature increased (Figure 3-6, bottom) to values as low as 40%. The phenomenon noticed in the composite sample separation was similar to what Rosen (1989) described as part of the complex effect of temperature on the CMC of surfactants. Rosen (1989) stated that, in an aqueous medium, the effect of temperature on the CMC first appears to decrease with temperature to some minimum, in this case 75°C, and then to increase with further increase in temperature. It is not known why the mass percentages decreased with increased temperature after the critical point, it is possibly due to the reduction of the volume of the organic-rich phase. This is supported by the fact the concentrations for target compounds continued to increase with increasing temperature in the composite volume samples (Figure 3-7, top). In the case of the 1<sup>st</sup> pore volume samples, the concentrations of the target analytes remained relatively constant as a function of temperature (Figure 3-7, bottom). Since the mass percentage decrease was not a function of the constituent composition in the organic-rich phase, it was most likely

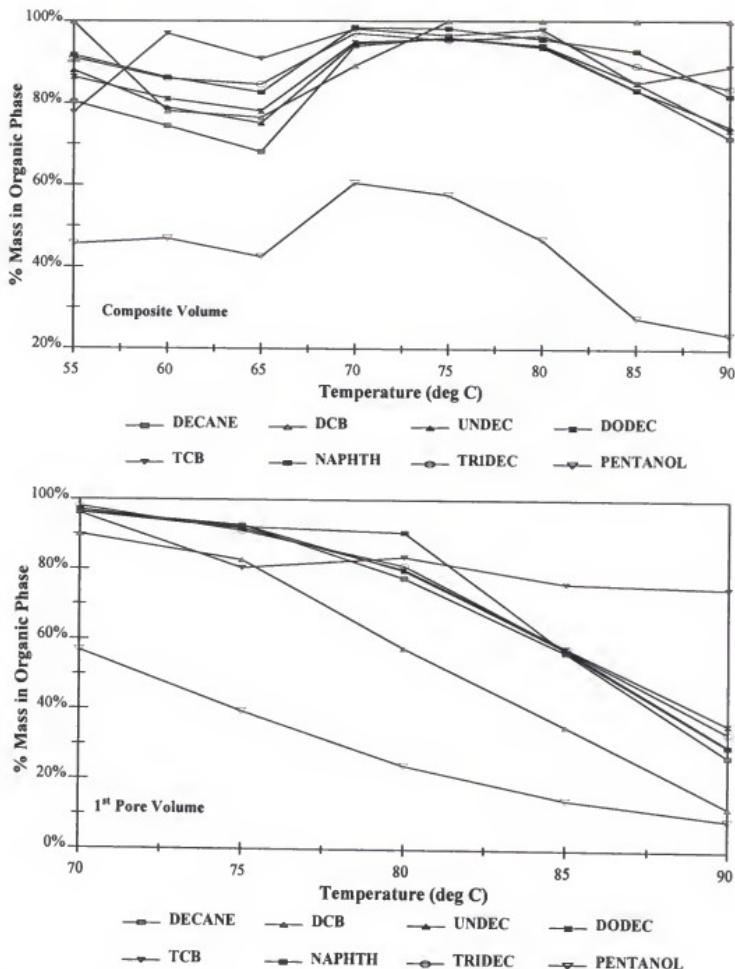


Figure 3-6 Percentages of target analyte mass partitioning into the separated organic phase as a function of the ambient temperature. Target analytes include: decane; 1,2-dichlorobenzene (DCB); undecane (UNDEC); dodecane (DODEC); 1,2,4-trichlorobenzene (TCB); naphthalene (NAPHTH); tridecane (TRIDEC); and pentanol.

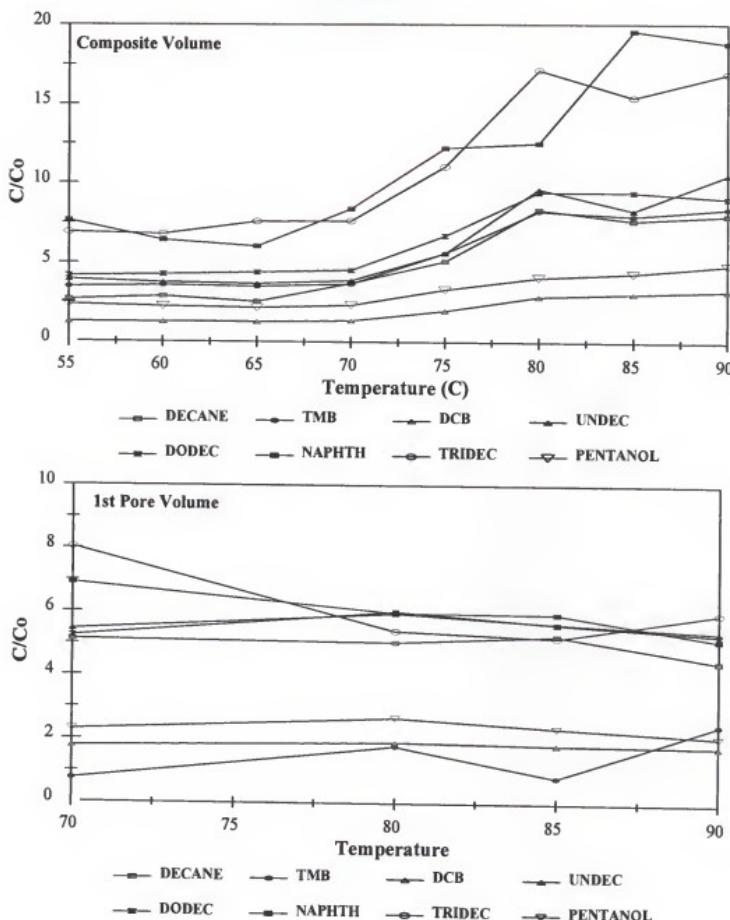


Figure 3-7 Relative concentrations ( $C/C_0$ ) of target analytes partitioning into the separated organic phase as a function of the ambient temperature. Target analytes include: decane; 1,2-dichlorobenzene (DCB); undecane (UNDEC); dodecane (DODEC); 1,2,4-trichlorobenzene (TCB); naphthalene (NAPHTH); tridecane (TRIDEC); and pentanol.

due to the decrease in the volume of the separated phase itself. It was also likely that some of the NAPL constituents volatilized into the sample headspace at the higher temperatures due to their low vapor pressures. The reaction of pentanol mass percentages at the different temperatures was similar to that of the other target analytes.

Scaling the concentrations of the target analytes to their initial concentrations in the SPME waste effluent was conducted to determine the relative change in composition as a function of separation temperature (Figure 3-7). The relative concentration ( $C/C_0$ ) of the NAPL target analytes in the organic-rich phase of the composite volume samples gradually increased as a function of temperature increase. On the other hand, the relative concentration of the target analytes in the organic-rich phase of the 1<sup>st</sup> pore volume samples remained relatively constant with change (increase) in ambient temperature. The relative concentration of the composite volume follows the pattern of the volumetric separation of the SPME noted in Figure 3-5. Before 75°C, the relative concentration and the volumetric separation were both fairly constant. After this point, as the organic-rich volume decreased, the concentration of target constituents increased. This would be a logical conservation of mass as the amount of the constituents was compressed into a smaller volume, their concentration in that volume should increase. However, as mentioned earlier, the concentration of the target analytes into the smaller volume was not totally proportional, as the mass percentages of the components in the organic-rich phase decreased with increasing temperature. In the 1<sup>st</sup> pore volume sample, despite the decrease in the separated organic-rich phase, the relative concentrations remained comparatively constant. Apparent conservation of concentration resulted in that as

temperatures increased, mass percentages decreased in the organic-rich phase while the volume of the phase decreased. A relatively constant concentration would support a simultaneous decrease in volume and mass in the separated organic-rich phase.

The composite volume and 1<sup>st</sup> pore volume samples differ in the partitioning of pentanol into the organic-rich phase after separation as a function of temperature in the same manner displayed in the partitioning of the target analytes. In the composite volume sample, the concentration of pentanol in the organic phase remained nearly constant until about 75°C (Figure 3-7, top), after which, the concentration gradually increased, as mass percentages recovered decreased. Conversely, in the 1<sup>st</sup> pore volume sample, the pentanol concentration in the organic-rich phase remains basically constant over the range of temperatures, as mass percentages recovered and volume of organic-rich phase decreased (Figure 3-7, bottom).

Conservation of different phase characteristics seem to be the difference between temperature separation of the composite volume and 1<sup>st</sup> pore volume samples. For the 1<sup>st</sup> pore volume sample, the concentration of target analytes seemed to be conserved during phase separation by temperature. While for the composite volume sample, the mass of the target analytes was generally conserved as a function of temperature separation.

#### Brij 97

The analysis of surfactant was difficult because of its component breakdown after phase separation. A qualitative estimate of the surfactant concentration was utilized based on the presence of a signature peak on GC chromatograms. Based on the initial concentration of Brij 97 (30,000 mg/L) in the SPME solution, it was shown that

increasing the temperature led to a partitioning of the Brij 97 into the upper organic-rich phase for composite volume sample (Figure 3-8), as expected based upon the literature (Kahlweit et al., 1989; Rosen, 1989). For the temperatures of 70°C, 80°C, and 90°C, the concentrations of Brij 97 in the organic-rich phase of the composite volume sample were found to be ~14,500 mg/L; ~32,000 mg/L; and ~35,000 mg/L, respectively. In the 1<sup>st</sup> pore volume samples, on the other hand, the surfactant basically divided evenly into the separate phases with out any respect to changes in temperature (Figure 3-8). The concentration of Brij 97 remained basically 15,000 mg/L in the organic-rich phase of the 1<sup>st</sup> pore volume sample. The volume of the organic-rich phase was smaller than the separated aqueous-rich phase, so the surfactant was more concentrated in the organic-rich phase. The resulting surfactant partitioning into the organic-rich phases of both sample sets seemed to reflect what was seen in the partitioning of the target analytes. The conservation of surfactant amount (mass) occurred in the composite volume sample, while conservation of concentration occurred in the 1<sup>st</sup> pore volume samples. Residual amounts of the surfactant in the separated aqueous-rich phases were attributed the hydrophilic portion of Brij 97 which remained more soluble in the aqueous-rich phase compared to the organic-rich phase.

#### COD

Chemical oxygen demand (COD) readings were conducted on the separated aqueous-rich phases. The COD concentrations for the SPME effluent waste was found to be 126,000 mg/L and 120,000 mg/L for the 1<sup>st</sup> pore volume and composite volume samples, respectively. Increasing the ambient temperature resulting in phase separation

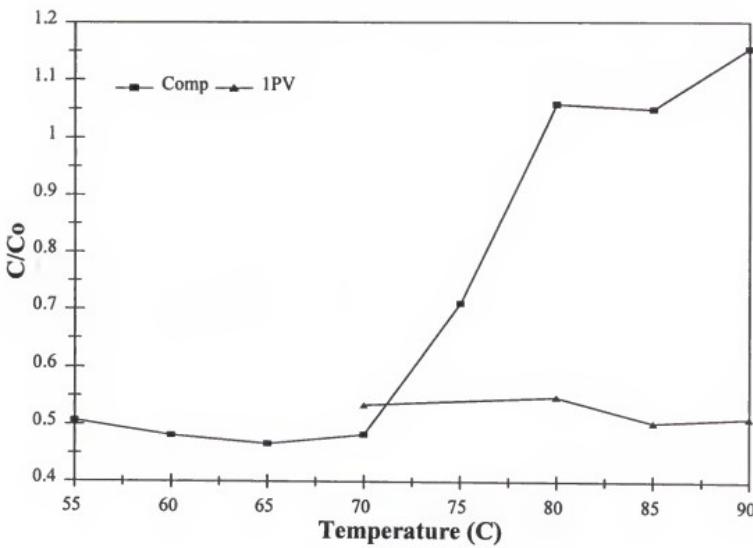


Figure 3-8 Relative concentrations of Brij 97 surfactant present in the separated organic phase in the composite volume and 1<sup>st</sup> pore volume samples as a function of temperature

reduced the COD concentrations found in the remaining aqueous-rich phases for both sets of samples dramatically. The COD concentrations went as low as 34,000 mg/L and 30,000 mg/L for the composite and 1<sup>st</sup> pore volume samples, respectively. With increasing temperature, the COD concentration in the aqueous-rich phase of the composite volume sample was seen to decrease initially and then began to increase after the 70°C point. While in the 1<sup>st</sup> pore volume sample, the COD concentration increased after its initial phase separation point of ~ 70°C (Figure 3-9). Both of these trends agree with those of pentanol found in the aqueous phases (Figure 3-10), conceivably because pentanol has been found to constitute up to and over 99% of the COD load in these separated aqueous-rich phases. This relationship emulates the close relationship shown between the COD and pentanol concentrations for salt phase separation seen in Chapter 2.

Elevated temperatures were shown to cause effective phase separation which reduced the volume of solution saturated with NAPL. However, this phase separation was not directly a function of increasing temperature. Most field generated wastes would most likely be similar to the composite volume sample. Even though the composite volume sample displayed optimal behavior at the highest applied temperatures for volumetric separation and relative concentration values, the mass percentage partitioning into the organic-rich phase did not emulate this behavior. Nonetheless, the mass separation for the target compounds into the organic-rich phase was generally greater than 80%. In conclusion, the highest ambient temperature did not give the most optimal or desired phase separation results in the case of this surfactant mixture. Therefore, optimization experimentation should be conducted when applying this phase

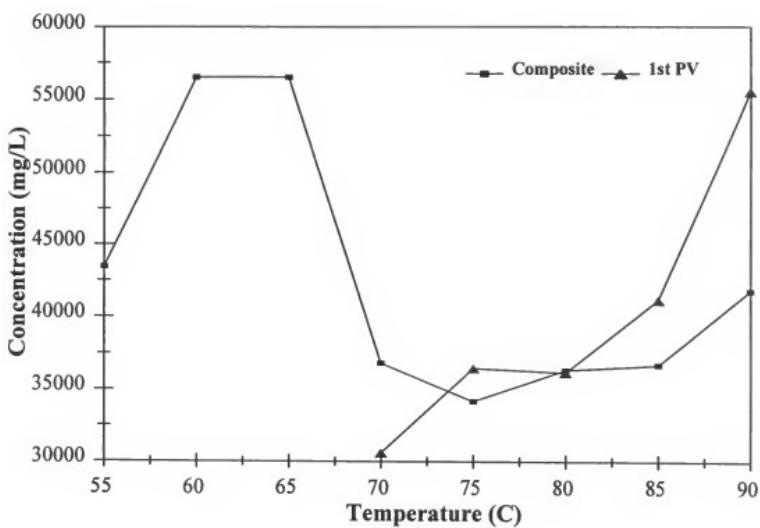


Figure 3-9 COD concentration present in the separated aqueous phase of the composite volume and 1<sup>st</sup> pore volume samples as a function of the ambient temperature

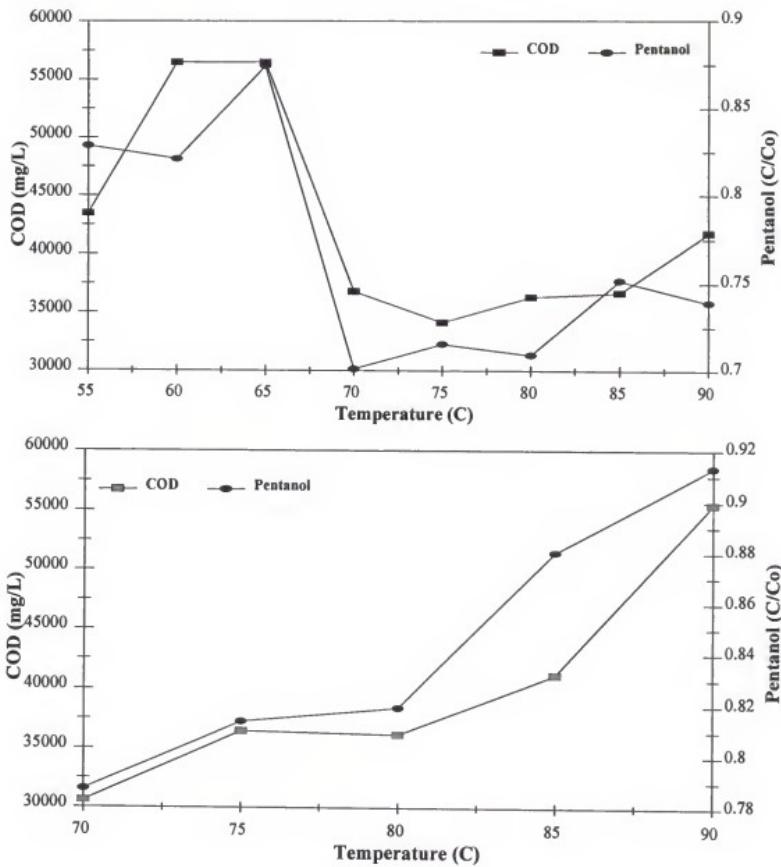


Figure 3-10 Comparison between the relative concentration of pentanol and the COD concentration in the separated aqueous phase as a function of the ambient temperature of the composite volume sample (top) and the 1<sup>st</sup> pore volume sample (bottom).

separation method to a different SPME effluent mixture.

### Conclusions

The purpose for this study was to investigate the effectiveness of an intermediate treatment process of phase separation by elevating temperatures of an SPME waste effluent taken from a subsurface remediation process. Incorporation of this procedure could be used to reduce the amount of waste that would require expensive treatment by methods including incineration. Based on experimental results, increasing temperature was found to produce significant immiscible phase separation of the initial effluent microemulsion.

For a constant temperature, 70°C, it was found that volumetric separation was essentially constant for samples taken over the length of the subsurface flushing experiment and that there was no preferential partitioning of the target components into the separated organic-rich phase.

Volumetric separation of the composite volume and 1<sup>st</sup> pore volume samples both increased as a function of increasing temperature. In this analysis, the aqueous-rich phase volume after separation increased as temperature applied to the SPME waste increased. Although the composite volume sample displayed phase separation at a lower temperature (55°C) than the 1<sup>st</sup> pore volume sample (70°C), the optimum separation fraction was the same, 0.96 (ratio of aqueous volume to total SPME volume). Beyond a temperature of 90°C, the level of volumetric separation of the SPME did not improve.

Percentages of mass of the NAPL target components partitioning into the organic-rich phase of the composite volume sample seemed to decrease after initial separation and then steadily began to rise to maximum values around 75°C, and then decreased again. Despite this behavior, the mass percentages partitioning into the separated organic-phase of the composite volume samples were generally greater than 80%. For the 1<sup>st</sup> pore volume, after initial separation at 70°C, mass percentages of the targeted NAPL analytes partitioning into the organic-rich phase decreased rapidly to values as low as ~40% as temperature increased.

Relative concentrations for target compounds increased with increasing temperature in the composite volume samples, while for 1<sup>st</sup> pore volume samples, the concentrations of the targeted analytes remained relatively constant as a function of temperature. These trends were also emulated by pentanol and Brij 97 behavior as a function of temperature separation.

COD concentration was found to be closely related to the amount of pentanol in the separated aqueous phase. This was because the majority of the COD concentration (~99%) was attributed to the presence of pentanol in solution.

Conservation of different phase characteristics seems to be the difference between temperature separation of the composite volume and 1<sup>st</sup> pore volume samples. For the 1<sup>st</sup> pore volume sample, the concentration of target analytes seemed to be conserved, however for the composite volume sample, the mass of the target analytes was relatively conserved as a function of temperature separation.

CHAPTER 4  
WASTE MANAGEMENT OF A MICROEMULSION USING  
ELECTROLYTE ADDITION AT ELEVATED TEMPERATURES

Introduction

Remediation of hazardous waste contaminated sites is a topic of major importance in the environmental field. The implementation of in-situ flushing with either surfactants or cosolvents or mixtures of the two have shown effective removal of NAPLs from contaminated aquifers through NAPL enhanced solubilization (West and Harwell, 1992; Chevalier et al., 1997; Pennell et al., 1997; Rao et al., 1997; Jawitz et al., 1997). Such remedial techniques aid in removing the contamination from the subsurface, but research on how to manage the resulting hazardous effluent still needs to be conducted. Presently, incineration is usually employed, however, the cost of this procedure has been shown to be very expensive and can be responsible for between 45 and 75% of the total site remediation expenditure (Perdek, 1997). The introduction of intermediate processes in treating the waste may aid in reducing the volume waste that would require expensive incineration. This research focuses on an inexpensive, yet effective, intermediate step of salt addition at elevated temperatures that may be used to reduce the amount of waste that would need treatment, disposal, or the amount of work needed to recycle chemical agents from it. Reduction of costs incurred for treatment or energy required should reduce the

total expenditures for waste treatment after site remediation, thereby improving overall project efficiency.

The purpose of this research was to examine the intermediate treatment process of adding an electrolyte (NaCl) at increased temperatures to a single phase microemulsion (SPME) effluent from a surfactant/cosurfactant flushing test conducted at a field site. Independently, the addition of salt and the increasing of ambient temperature each will cause the SPME to separate into two immiscible phases due to phase inversions in the microemulsion (Menon and Wasan, 1985). It is believed that a combination of these methods would allow for a synergistic effect resulting in a more efficient separation of the SPME effluent requiring lower amounts of salt and lower temperatures. The effluent SPME is the result of surfactant flushing of an isolated subsurface test cell at Hill AFB, Utah in an field experiment described by Jawitz et al. (1998). As listed in previous chapters, the site, the precursor solution, and the resulting Winsor Type I SPME solution has been documented in the literature (Montgomery Watson, Inc.,1995; Rao et al., 1997; Rhue et al., 1997; Jawitz et al., 1998; Annable et al., 1998). The flushing solution consisted of 3.0% by weight of the surfactant named polyoxyethylene-(10)-oleyl-ether (trade name Brij 97) and 2.5% by weight of n-pentanol as the cosurfactant.

### Background

Discussions of the individual effectiveness of salt and increased temperatures on phase equilibrium in microemulsion systems have been explored in previously published literature as seen in the previous two chapters. The addition of salts have had definite

impacts on the solubility of organic compounds in amphiphilic systems (Kahlweit et al., 1984; Kahlweit et al., 1985; Kahlweit et al., 1989; Sassen et al., 1989; Kahlweit et al., 1990; Wilcoxon, 1990; Kunieda and Nakamura, 1991; Kabalnov et al., 1995). The effects of temperature on the phase stability of microemulsions has also garnered significant research attention (Menon and Wasan, 1985; Rosen, 1989; Kahlweit et al., 1990; Alexandridis et al., 1995; Kabalnov et al., 1995).

Theoretical background describing the combined effects of salt and temperature upon emulsion systems have also been provided in the literature. The addition of a lyotropic salt, such as NaCl, to a nonionic surfactant was found to cause a drop in the temperatures required to produce a phase transition (Kahlweit et al., 1985; Kahlweit et al., 1989; Kahlweit et al., 1990; Clark et al., 1999). Kahlweit et al. (1985) showed that since adding lyotropic salts shift the phase change regions to lower temperature ranges, then the addition of NaCl would require less temperature to be added to a system to cause the nonionic surfactant to partition into the upper oil-rich phase of an immiscible two-phase system. This differs from reaction of ionic surfactants, where these temperature ranges rise. The effect on the ionics is determined by the ionic strength of the brine (salt/water solution), regardless of the nature of the anions. However, where the nonionics are concerned, the effect of the lyotropic salts depend upon the nature of the anions or the Hofmeister series, which was mentioned in Chapter 2. Firman et al. (1985) studied the lyotropic series and provided values for the relative strengths of electrolytes in the presence of nonionic surfactants and their dependence upon ambient temperature.

Rosen (1989) adds that nonionic surfactants are subject to coacervation at increased temperatures, which refers to the formation of a separate surfactant-rich phase at the cloud point. This possible cloud point is lowered by the addition of salt to the SPME effluent, which provides for easier separation at lower temperatures. Kahlweit et al. (1990) and Clark et al. (1999) similarly concluded that for a given nonionic surfactant combined with oil, increasing the salt concentration decreases the temperature required to cause a separation of phases (Figure 3-1, middle). Kahlweit et al. (1990) additionally concluded that for a given oil, as the hydrophobicity of the nonionic surfactant increases, the separation temperature of the microemulsion again decreases; and, also, as the carbon number of a solubilized oil increases for a given nonionic surfactant, the separation temperature increases.

Kahlweit (1995) additionally discussed that the increase of temperature causes the nonionic amphiphile to be distributed more into the oil-rich phase than the aqueous-rich phase. Kahlweit continued by describing how nonionic amphiphiles may be “salted-out” of solution. He reported that a salt-free solution would require the highest temperature to initiate the partitioning of the nonionic surfactant into the oil phase of a separated two phase system. Kabalnov et al. (1995) and Kahlweit (1995) also showed that with increasing salt concentrations, lower temperatures would be required to partition the nonionic surfactant into the separated oil phase (Figure 4-1). In Figure 4-1, Kahlweit (1995) displays the tendencies of nonionic and ionic surfactants to partition into the upper oil-rich phase ( $\bar{2}$ ), the lower aqueous-rich phase ( $\underline{2}$ ), or the 3 phase region as a function

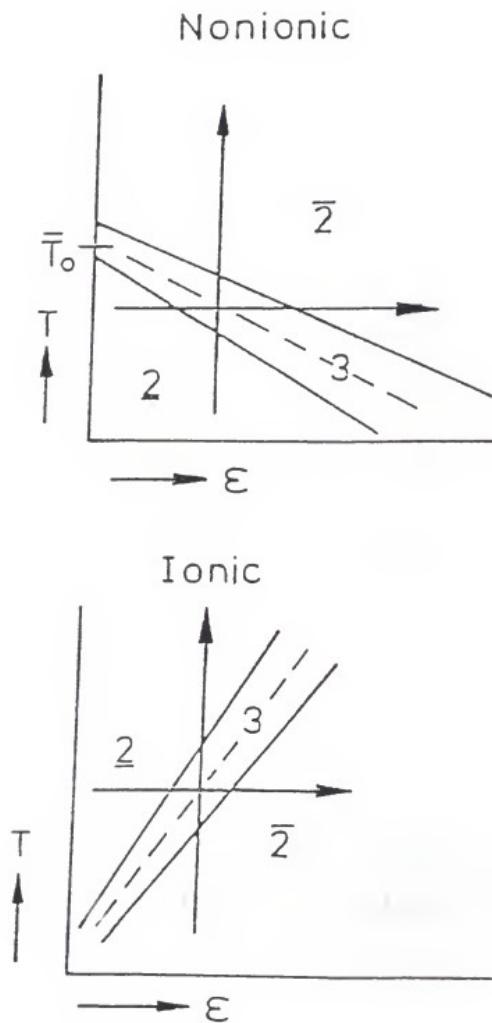


Figure 4-1 Partitioning of nonionic (top) and ionic (bottom) surfactants into immiscible separated phases as a function of temperature and salt concentration ( $\epsilon$ ). (Kahlweit, 1995)

of temperature and salt concentration ( $\epsilon$ ). As the nonionic surfactant is partitioned into the upper oil-rich phase, the solution becomes a water-in-oil (w/o) dispersion denoted by the term Winsor II system. Kahlweit et al. (1990) and Kahlweit (1995) went on to state that with a fixed salt concentration, continuous raising of the temperature would transform the oil-in-water (o/w) emulsion (Winsor I) to a three phase system (Winsor III) to a w/o emulsion (Winsor II). These articles also stated that although medium and long-chain alcohols added as cosurfactants lower the amount of salt and temperature required to produce the phase transformations, they also tend to form weak structures that cannot be easily represented upon a 3-D phase diagram. The increase of salt at a constant temperature was also noted by Bourrel and Chambu (1983) to provide the same Winsor I-II phase transition. Kabalnov et al. (1995) went on to conclude that adding a depleting salt species (lyotropic) to a surfactant monolayer dehydrates its hydrophilic portion through an osmotic equilibrium. This leads to a curvature shift towards water, and facilitates the transition to a w/o microemulsion.

The objectives of this study were: 1) to investigate the effects of adding various salt concentrations in combination with elevated temperatures to a field generated SPME and how different combinations of each would affect the separation efficiency of the solution into organic-rich and aqueous-rich phases; 2) to investigate the partitioning of the NAPL removed in the SPME into the organic-rich phase as a function of the salt concentration and ambient temperature; and 3) to compare the effectiveness and efficiency of these intermediate treatment combinations when applied to sample volumes taken at different periods in the in-situ flushing process.

### Materials and Methods

Experimental samples were taken periodically from the effluent of the combined extraction wells from the surfactant flushing in a test-cell located at Operable Unit-1 (OU-1) at Hill Air Force Base, Utah. The experiment analyzed SPME samples of the composite waste fluids that were taken from the cumulative effluent from the entire flushing experiment, and also after the first pore volume in the subsurface was displaced. The effect of salt addition on the SPME waste was evaluated using various weight percentages (0.1 - 10% by weight) added to 10 mL volumes of SPME waste in KIMAX® centrifuge tubes which were then placed in a constant-temperature water bath over a range of temperatures (23 - 60°C) for time periods of a minimum of 15 minutes to no longer than 30 minutes. The maximum of the explored temperature range was defined based on the fact that phase separation of the SPME effluent occurred between 65-70°C when no salt was added to the solution.

After phase separation, an aliquot of the upper organic layer was diluted (1:10) in methylene chloride ( $\text{MeCl}_2$ ) and was batch extracted on a rotary shaker for ~2 days to allow equilibrium to be reached (Chen et al., 1996). The  $\text{MeCl}_2$  solution and the aqueous phase were both analyzed by GC-FID for target analytes and the cosurfactant, pentanol.

A Perkin-Elmer Gas Chromatograph (GC), equipped with a Flame Ionization Detector (FID) and a DB-624 column, was used to analyze the microemulsion waste and the  $\text{MeCl}_2$  dilutions of the oil phases for pentanol and target NAPL analytes. The target analytes are the same as in previous chapters, which were selected by Rhue et al. (1997), and included p-xylene, 1,2,4-trichlorobenzene, 1,2,4-trimethylbenzene, n-decane, n-

undecane, n-dodecane, and n-tridecane.

Chemical oxygen demand (COD) tests were conducted based on the EPA approved (Federal Register, 1980) Reactor Digestion Method 8000 found in DR/2000 HACH Spectrophotometer Handbook with HACH High Range Plus COD Reagent (Loveland, CO). The high level wastes were also analyzed with colorimetric determination with a Milton Roy Spectronic 21D Spectrophotometer.

#### Results and Discussion

Effluent from the SPME subsurface flushing experiment, which took place at Hill AFB, Utah (Jawitz et al., 1998 and Clark et al., 1997), was used to determine the effectiveness and efficiency of an intermediate treatment process which combined the addition of salt at elevated temperatures. The evaluation of these combined treatment procedures were based upon volumetric phase separation, mass partitioning of target NAPL constituents, and chemical oxygen demand (COD) concentrations of resulting aqueous phase. As initially stated in Chapter 2, the effectiveness of phase separation was evaluated based on the value of the volumetric separation ratio. As this value grew closer to 1, the parameters at each level of phase separation were more effective in removing the surfactant and hydrophobic contaminants from the separated aqueous phase. The efficiency of phase separation was dependent on the minimal amounts of salt added and/or minimal elevation of the temperature that was required to achieve particular levels of effective phase separation, especially when these parameters were used together.

As shown in Figure 2-1, it was concluded that the components were not preferentially removed during in-situ flushing procedure. Therefore, for the various analyses used in evaluating the addition of salt at increased temperatures, the samples were relatively consistent in composition.

#### Volumetric Separation

As previously stated, the volumetric phase separation was evaluated on the basis of taking a ratio of the volume of the remaining aqueous-rich phase after phase separation to the volume of the SPME waste prior to phase separation. Inspection of the volumetric separation curves (Figure 4-2) showed that for both composite volume and 1<sup>st</sup> pore volume samples, as temperature increased, less salt was required to reach an optimum separation level. This was evidenced by sharper slopes for each increasing temperature curve, which indicated that smaller concentrations of salt were required to reach a level of volumetric phase separation. This suggested that elevation of temperature increased the efficiency of phase separation based on minimizing the amount of salt that was required to be added to the SPME effluent to achieve similar volumetric separation ratios. These results agreed with conclusions made by Menon and Wasan (1985), Kahlweit et al. (1990), and Kahlweit (1995) concerning the effects of salt and temperature on a nonionic surfactant system. These conclusions stated that phase separation of nonionic microemulsions occur at lower concentrations of salt with increasing ambient temperatures, which was substantiated by experimental results gathered in this research.

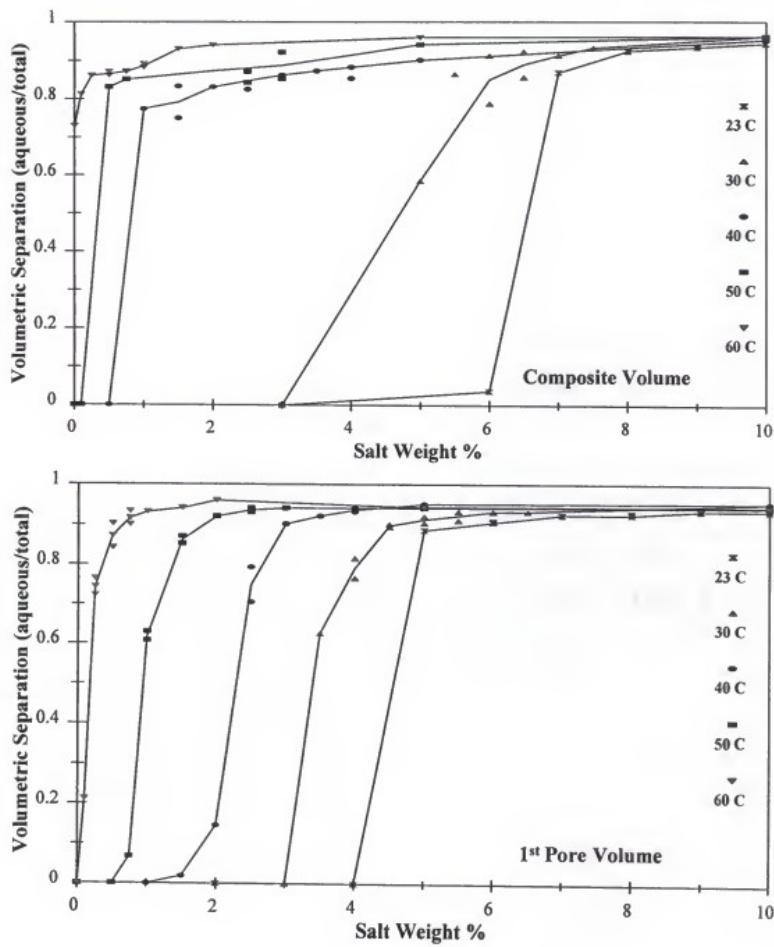


Figure 4-2 Volumetric separation of SPME effluent as a function of salt concentration and elevated temperature for the composite volume (top) and 1<sup>st</sup> pore volume (bottom) samples

For both sets of samples, ratios of the aqueous phase volumes compared to the total initial SPME volumes reached plateaus of separation effectiveness. These plateaus indicated that the effective separation capacity of the salt at each temperature had essentially reached a maximum; consequently, the addition of more salt would not have caused a significant improvement, if any, in the immiscible phase separation by volume. The beginning of these plateaus signified the maximum efficiency of the salt addition for separation due to the minimum salt added to achieve the optimum separation effectiveness. For the composite samples, the optimum separation in the temperature range from 23°C to 60°C occurred approximately around 0.96 (aqueous phase volume/total volume) as shown on Figure 4-2 (top). This indicated that the addition of salt at a given temperature caused the organic-rich phase, including surfactant and NAPL constituents, to be effectively concentrated to about 4% of the original SPME waste volume. For the 1<sup>st</sup> pore volume samples, the optimum level of separation was ~0.95 (Figure 4-2, bottom) for all of the elevated temperatures examined. Therefore, the effectiveness of separation based on volumetric phase separation ratio for the composite volume and 1<sup>st</sup> pore volume samples was basically the same.

At particular temperature levels, the composite volume samples generally required less salt to achieve similar volumetric separation when compared to the 1<sup>st</sup> pore volume samples (Figure 4-2). For the individual temperature levels, the composite samples initially broke close to their optimum volumetric separation fraction, however, the 1<sup>st</sup> pore volume samples increased in separation efficiency over a range of salt concentrations between the point of initial separation and the optimum fraction of

separation. This difference of separation can be explained by the composition of the two sample mixtures, which was demonstrated in a comparison of the amount of Brij 97 surfactant to pentanol.

The concentration ratio of surfactant to pentanol was 1.72 in the 1<sup>st</sup> pore volume samples, conversely, in the composite volume samples, this ratio was 1.25 . The maximum concentrations of the target analytes in the NAPL were eluted near the end of and after the 1<sup>st</sup> pore volume (~ 48 hours) flushed through the system (as seen in Figure 2-1); so, as flushing continued, water made up a larger portion of the SPME effluent. This would agree with the principle set forth by the surfactant/pentanol ratios, that the composite volume samples (taken from the cumulative effluent from the entire flushing experiment) contained a higher fraction of water than the 1<sup>st</sup> pore volume samples which were taken exclusively at the end of the 1<sup>st</sup> pore volume of the experiment. The hydroxide group in the pentanol is attracted to the water molecules in the bulk SPME solution due to hydrogen bonding (Snoeyink and Jenkins, 1980) and this attraction between the ionic groups in the SPME mixture leads to separation of the ionic and nonionic components in the micelles. Consequently, easier separation of the composite volume sample was due to the higher concentration of polar groups present in the system, which made it increasingly difficult for both ionic and nonionic constituents to remain together in a stable, single-phase microemulsion (Rosen, 1989; Kabalnov et al., 1995). This led to the coalescence of the organic phase trapped in the micelles. Therefore, the more water present in the SPME, the easier it was for salt to attract it away from the solubilized NAPL; and the less salt that was required to achieve separation of the

immiscible phases. This assertion seems to be indicative of what was seen in the results comparing the separation 1<sup>st</sup> pore volume and composite volume samples at various temperatures.

Volumetric separation data for each sample set at the various temperatures were combined to form three-dimensional surface diagrams with the aid of the Winsurf 5.0 program. This manipulation was conducted to attempt to interpolate the data between salt concentrations and temperature ranges examined in this study. The surfaces incorporated data gathered experimentally to attempt to display how phase separation, salt added, and temperature may be interrelated and a function of one another. Figure 4-3 displays the three-dimensional data for the composite volume and 1<sup>st</sup> pore volume sample sets. As shown previously on the two-dimensional figures (4-2), the optimum volumetric separation for the composite volume sample (denoted by light red shade) was seen more prominently than that of the 1<sup>st</sup> pore volume sample. The 1<sup>st</sup> pore volume sample showed a more gradual increase in the color red because it required more salt at different temperature levels to achieve near optimum separation values. Figure 4-3 basically provides a visual image of the phase separation that might be achieved for various combinations of salt concentrations and ambient temperature values for this particular SPME system. Other combinations of nonionic surfactants, cosurfactants, and contaminant compositions would expectedly provide similar, yet individually unique three-dimensional surfaces as functions of salt, temperature, and volumetric separation.

Data for separation of SPME based on the volumes of the immiscible phases after salt addition at elevated temperatures seems to indicate that this intermediate treatment

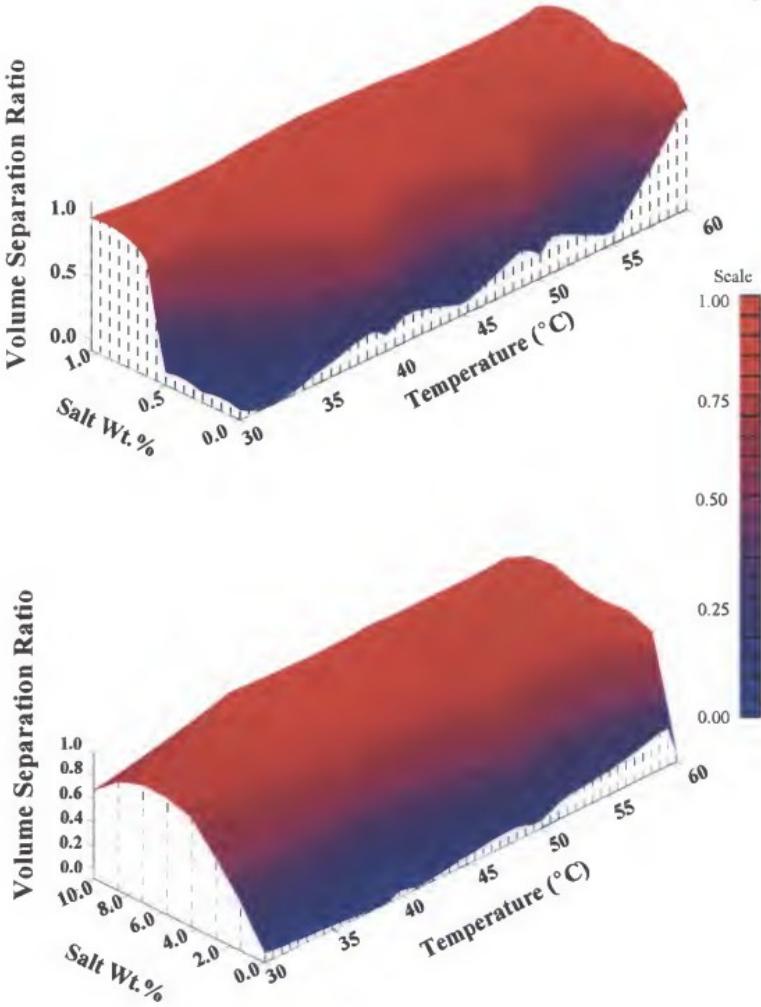


Figure 4-3 Surface representing volumetric separation of effluent SPME as a function of salt added for various temperatures in the composite volume (top) and 1st pore volume samples.

combination may reduce the volume of waste saturated with NAPL by up to 95%. This is an encouraging conclusion, however, other factors such as the mass partitioning of the NAPL into either phase must also be considered so that the usefulness of this method may be better understood.

#### Mass Partitioning

The mass partitioning percentages were evaluated for the target analytes and pentanol, and this reflected how much of the mass of the targeted analytes in the NAPL partitioned into particular separated phases. For example, it was shown that for undecane, >98% of its mass was found in the organic phase for various temperatures over a range of salt concentrations. The partitioning of this analyte was indicative of the range of mass partitioning that was seen for all of the targeted analytes examined in this study (Figures 4-4 and 4-5). This high level of mass partitioning was seen with relatively no difference between the composite volume and 1<sup>st</sup> pore volume samples. As far as the target analytes were concerned, there was no distinction made between mass partitioning percentages as a function of temperature. For all of the temperatures and salt concentrations studied, the mass partitioning percentages of the target analytes were generally greater than 95%. This leads to the deduction that as soon as phase separation occurs, the immiscibility of the hydrophobic target analytes in water almost completely drives them into the hydrophobic, organic-rich phase.

Pentanol partitioning into the organic-rich phase was also monitored as a function of temperature and salt. For the various temperatures investigated in this research, the partitioning of the pentanol mass was seen to increase with increasing weight percent of

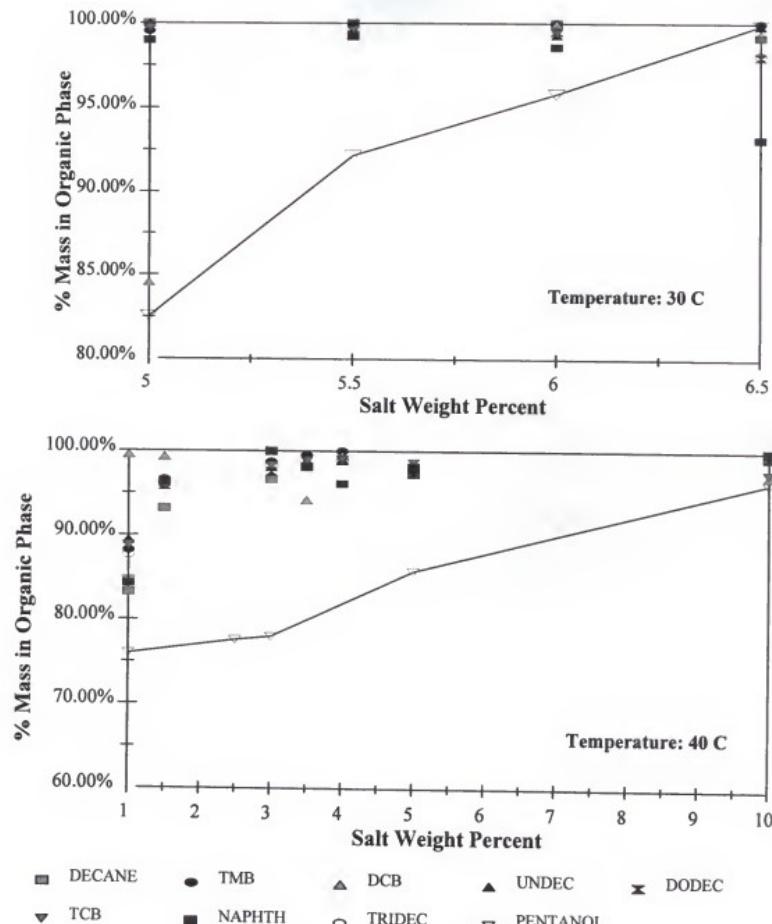


Figure 4-4 Percentages of target analyte mass partitioning into the separated organic phase of the composite volume sample as a function of salt concentration for various temperatures. Target analytes include: decane; 1,2,4-trimethylbenzene (TMB); 1,2-dichlorobenzene (DCB); undecane (UNDEC); dodecane (DODEC); 1,2,4-trichlorobenzene (TCB); naphthalene (NAPHTH); tridecane (TRIDEC); and pentanol.

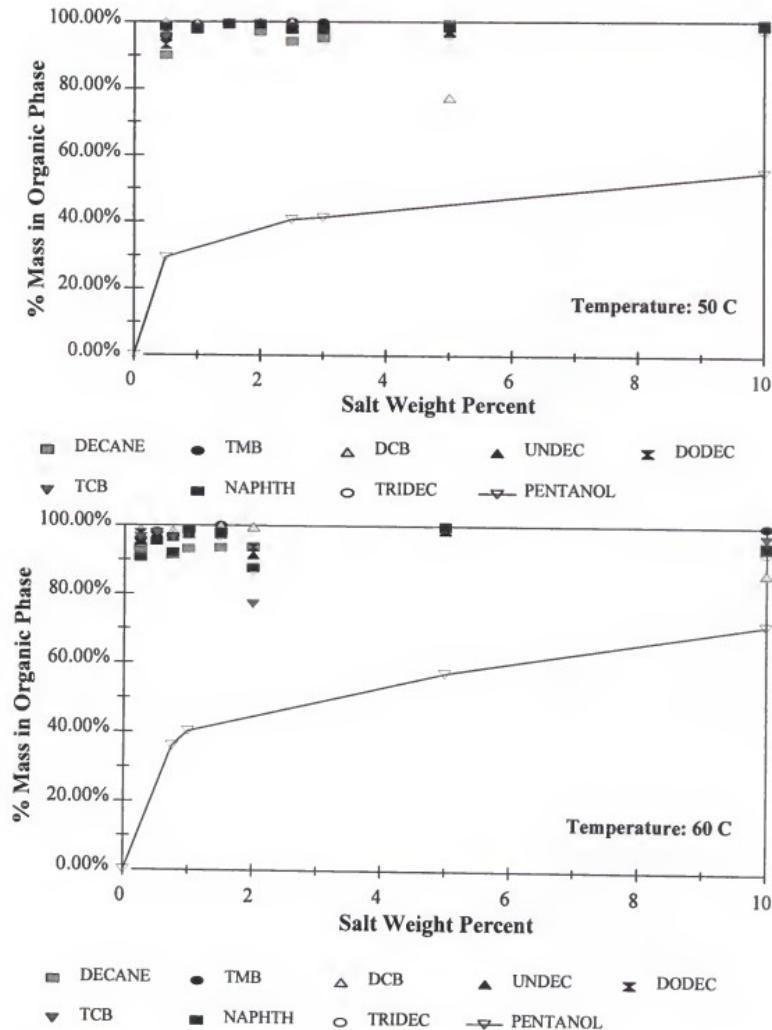


Figure 4-4 contd.

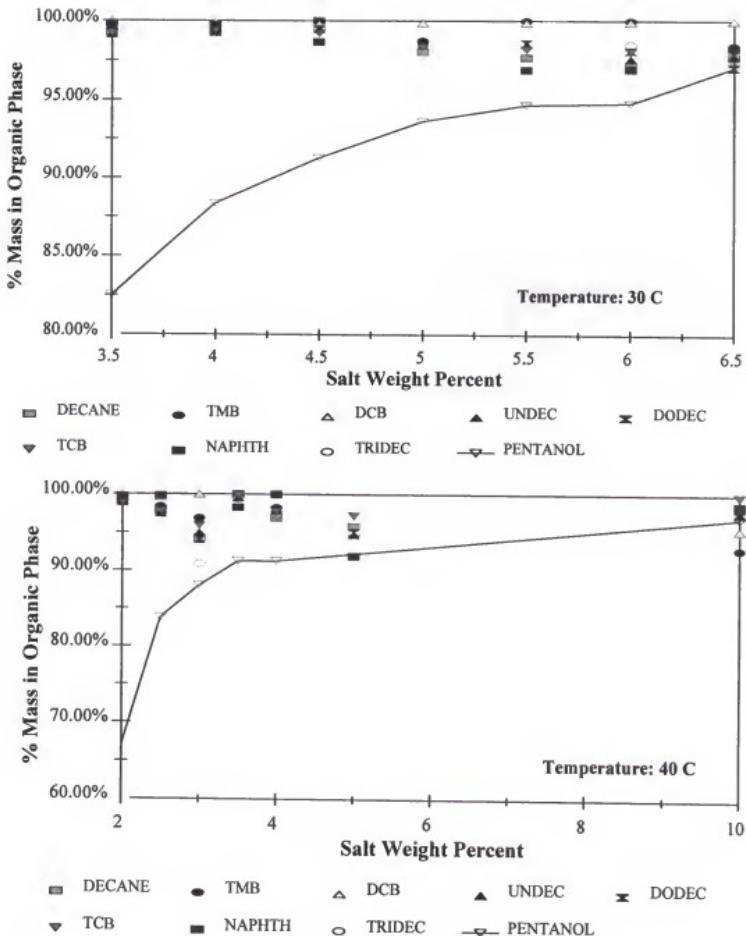


Figure 4-5 Percentages of target analyte mass partitioning into the separated organic phase of the 1<sup>st</sup> pore volume sample as a function of salt concentration for various temperatures. Target analytes include: decane; 1,2,4-trimethylbenzene (TMB); 1,2-dichlorobenzene (DCB); undecane (UNDEC); dodecane (DODEC); 1,2,4-trichlorobenzene (TCB); naphthalene (NAPHTH); tridecane (TRIDEC); and pentanol.

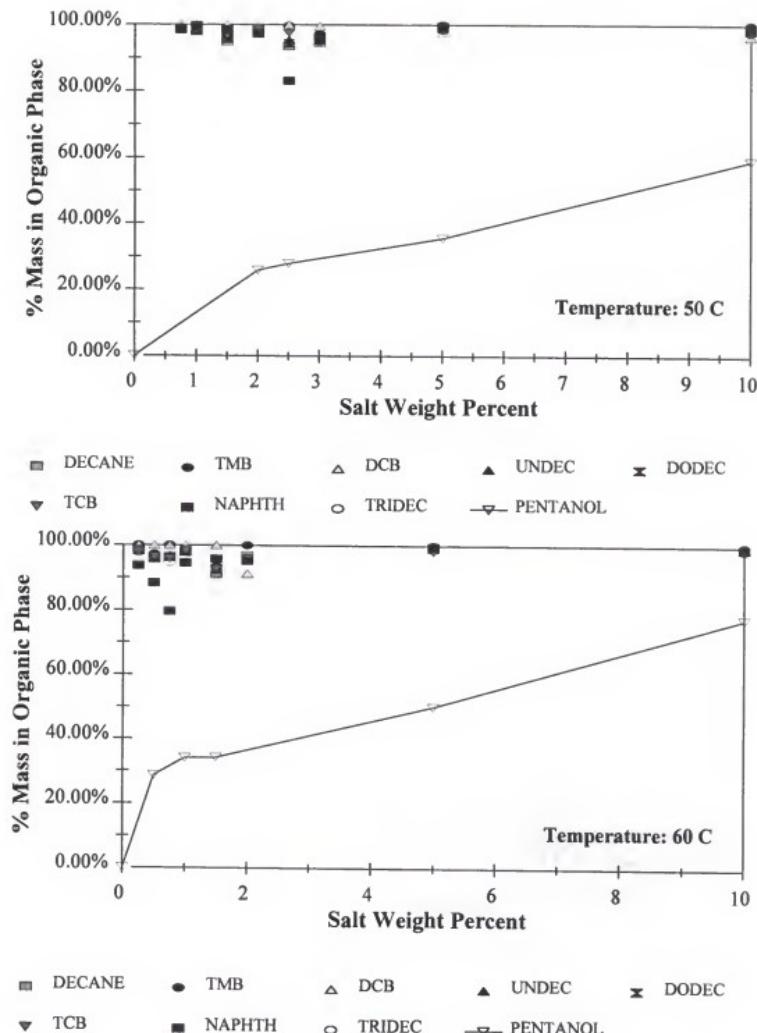


Figure 4-5 contd.

salt (Figures 4-4 and 4-5). Inspection of the pentanol data as a function of temperature indicated that as temperature increased, less pentanol was found to partition into the organic phase. In the composite volume sample, the highest mass percentages of pentanol that partitioned into the organic-rich phase were found in the high 90's at 30°C and generally decreased to the low 60's at 60°C. This trend was also mirrored in the 1<sup>st</sup> pore volume samples. As previously mentioned, in both samples sets the highest amounts of pentanol mass partitioning into the organic-rich phase occurred at the highest amounts of salt addition for all temperatures.

Scaling the concentrations of the target analytes to their initial concentrations in the SPME waste effluent was conducted to determine the relative change in concentrations as a function of ambient temperature and salt added (Figures 4-6 and 4-7). The relative concentrations (C/Co) of the NAPL target analytes and pentanol in the organic-rich phase of both composite volume and 1<sup>st</sup> pore volume samples gradually increased as the amount of salt added increased for all temperatures studied. This was expected since both the volume of the organic-rich phase continued to reduce while the mass partitioning into the organic-rich phase continued to marginally increase with increasing salt addition for all temperatures examined.

Examination of the relative concentration values as a function of temperature, however, did differ between the composite volume and 1<sup>st</sup> pore volume samples. As temperature was seen to increase at constant salt concentrations, the composite volume samples showed an increase in relative concentrations of target analytes, while for the 1<sup>st</sup> pore volume samples, these values remained comparatively constant. For example, at a

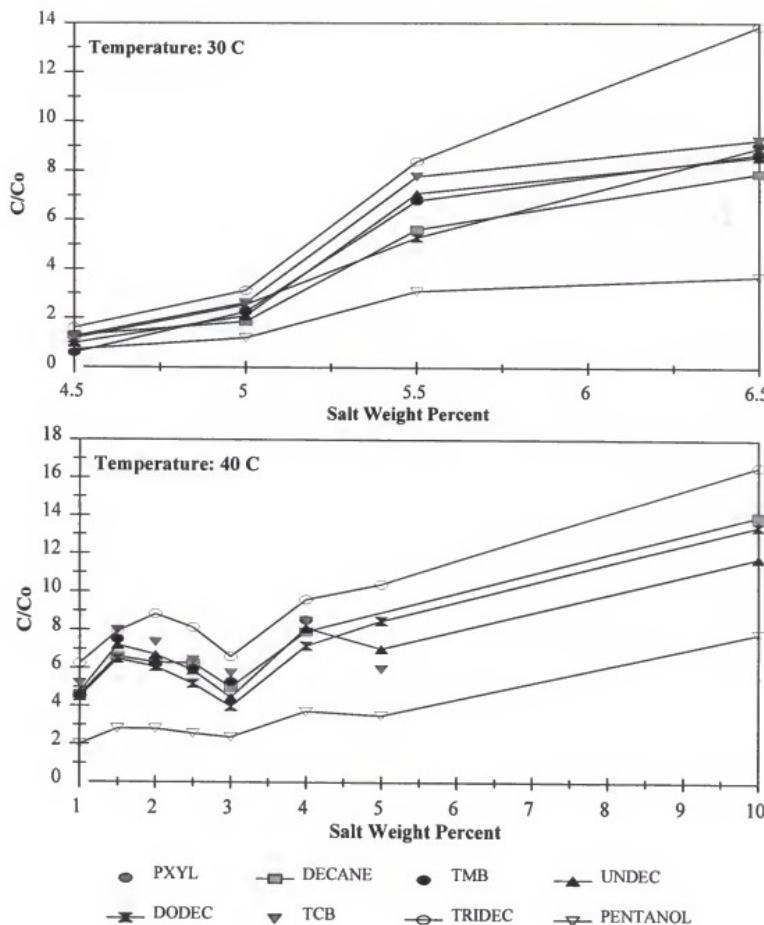


Figure 4-6 Relative concentrations ( $C/C_0$ ) of target analytes partitioning into the separated organic phase of the composite volume sample as a function of salt concentration for various temperatures. Target analytes include: p-xylene (PXYL); decane; 1,2,4-trimethylbenzene (TMB); undecane (UNDEC); dodecane (DODEC); 1,2,4-trichlorobenzene (TCB); tridecane (TRIDEC); and pentanol.

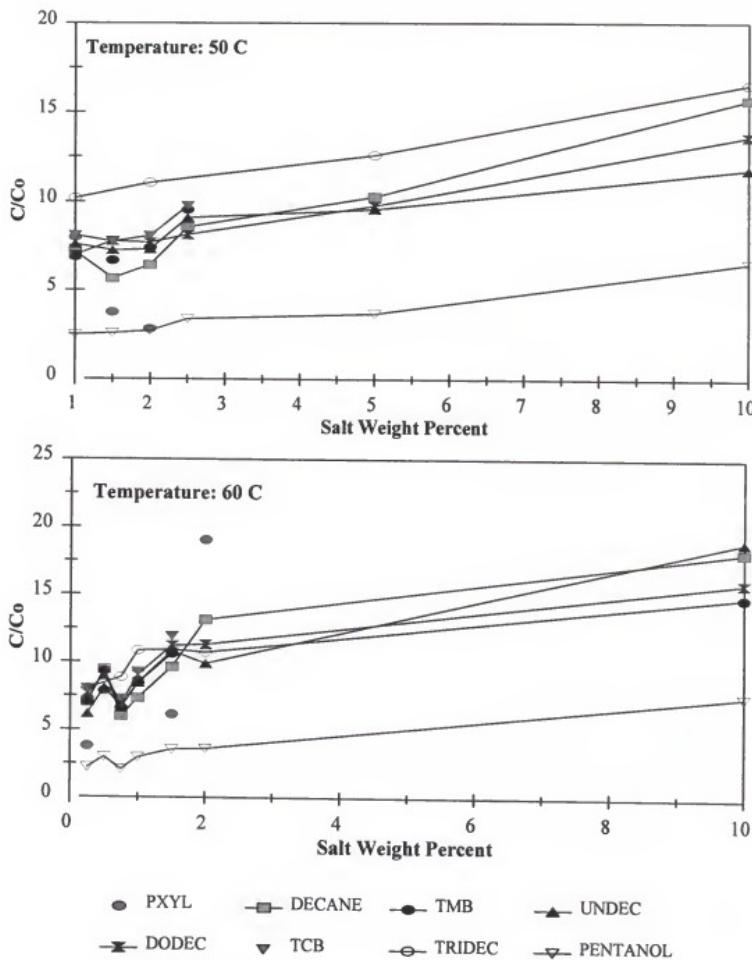


Figure 4-6 contd.

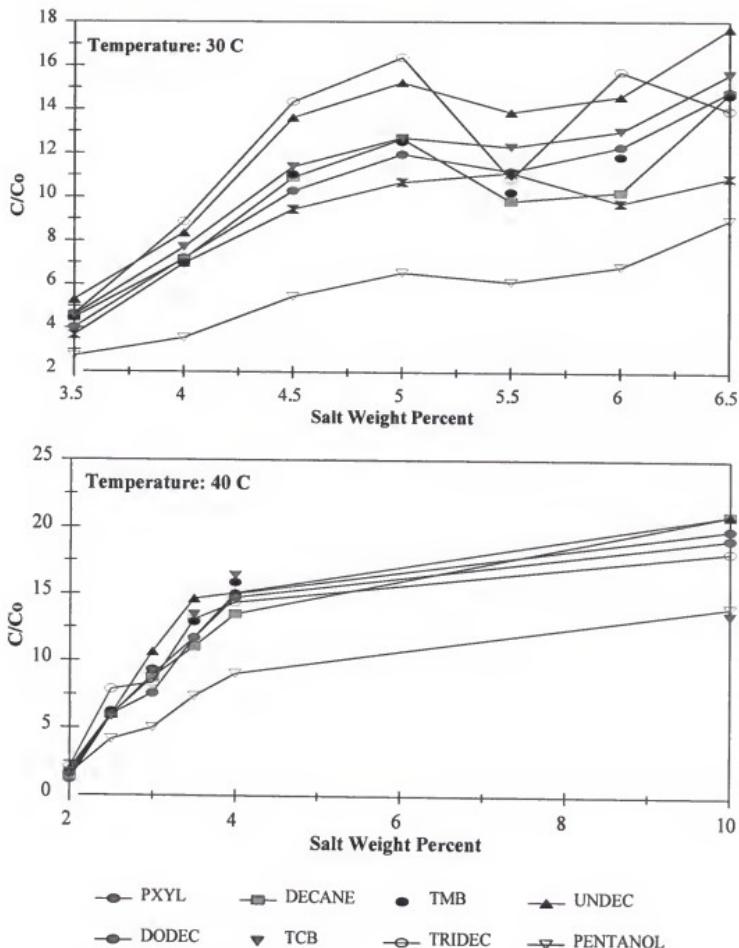


Figure 4-7 Relative concentrations ( $C/C_0$ ) of target analytes partitioning into the separated organic phase of the 1<sup>st</sup> pore volume sample as a function of salt concentration for various temperatures. Target analytes include: p-xylene (PXYL); decane; 1,2,4-trimethylbenzene (TMB); undecane (UNDEC); dodecane (DODEC); 1,2,4-trichlorobenzene (TCB); tridecane (TRIDEC); and pentanol.

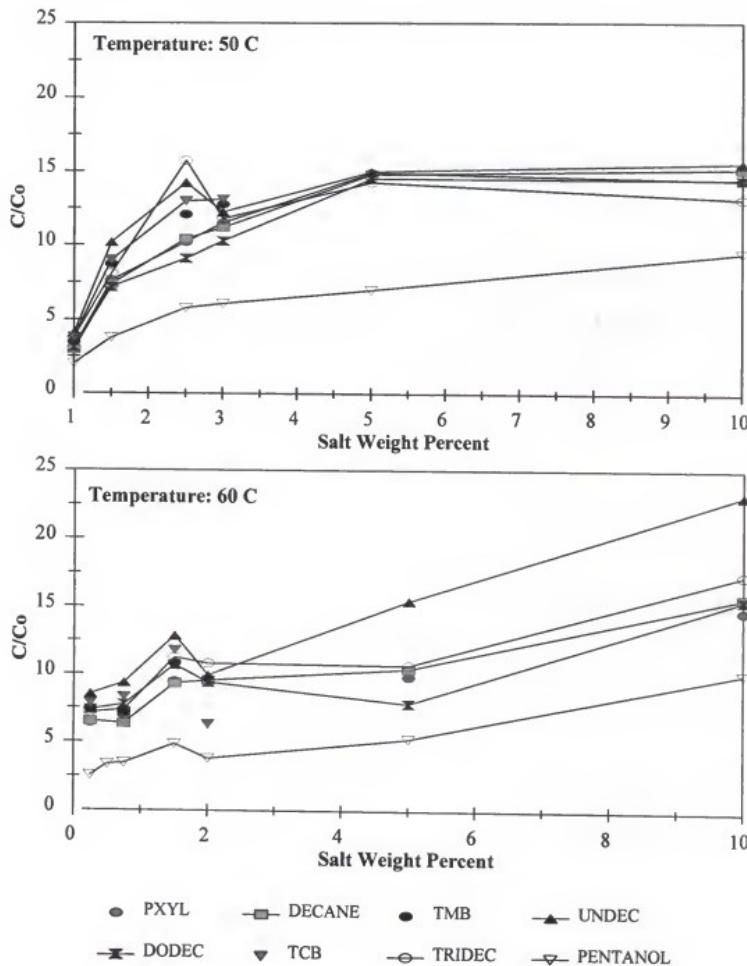


Figure 4-7 contd.

constant salt concentration of 5% by weight, the C/Co values for decane in the composite volume samples were 2.0, 8.0, 10.3, and 26.5 for the temperatures of 30°C, 40°C, 50°C, and 60°C, respectively (Figure 4-6). For this same temperature range, the C/Co values of decane in the 1<sup>st</sup> pore volume samples were basically in a range approximately from 11 to 15 (Figure 4-7). This phenomenon was similar to what was seen in study of temperature separations in the previous chapter. The composite volume samples seem to display a relative conservation of mass, where the concentrations increase as the volume decreases in reference to analytes partitioning into the organic-rich phase. Conversely, the 1<sup>st</sup> pore volume samples seem to display a general conservation of concentration because despite the decrease in the organic-rich phase volume, the C/Co values remained relatively constant. Apparently dependent upon temperature increase with or without salt, the composite volume samples display, for the most part, a conservation of mass; while the 1<sup>st</sup> pore volume samples conserve concentrations of analytes in the for all organic-rich phases after separation.

The composite volume and 1<sup>st</sup> pore volume samples differ in the partitioning of pentanol into the organic-rich phase after separation as a function of temperature in the same manner displayed in the partitioning of the target analytes, although on a lower value scale. Pentanol's lower partitioning values into the organic-rich phase could be attributed to pentanol's high aqueous solubility and low vapor pressure. However, this component could be extracted from the remaining aqueous phase by implementing simple evaporative and condensation techniques.

The high rate of mass partitioning and low organic-rich phase volumes after separation seemed to indicate that salt addition at elevated temperatures is an feasible intermediate method of handling waste. The volumes of NAPL-dominated waste were shown to be reduced by 95% based on volumetric separation ratios, while mass partitioning percentages indicated that usually greater than 98% of the target analytes partitioned into this reduced volume. This combination has worked to reduce the amount that would have to receive hazardous waste treatment, and, therefore, reduce the cost of these expensive treatment measures.

#### Brij 97

Similar to what was seen in the experiments described in the previous chapters, the addition of salt and temperature to the SPME effluent resulted in the break-down of the Brij 97 surfactant, and it no longer held a consistent analytical composition. Consequently, quantification of the total surfactant was not found to be reliable, however, use of GC analyses located a peak in the original surfactant chromatogram was found to persist more than any other component after separation. This signature peak was used to semi-quantitatively estimate, by initial concentration ratio, the amount of Brij 97 present in each phase. Based on the condition that 30,000 mg/L was the initial concentration of Brij 97 in the SPME solution, the use of the signature peak led to certain conclusions about the partitioning of the surfactant into the two immiscible phases.

In general, it was shown that increasing temperature at a constant salt concentration led to concentration of the Brij 97 into the upper organic-rich phase and away from the aqueous phase. For 5 wt.% salt added to the composite volume sample,

the concentration of Brij 97 in the separated organic phases were approximately 38,000 mg/L; 48,000 mg/L; and 85,000 mg/L for the temperatures of 40°C, 50°C, and 60°C, respectively. In the same respect, the Brij 97 concentrations in the composite volume aqueous phase for 5 wt.% salt addition were 5600 mg/L; 1400 mg/L; and < 675 mg/L for the same temperatures. These results agreed with the conclusions made by Kahlweit et al. (1990), which stated that at elevated temperatures, the nonionic surfactants are more soluble in the oil-rich phase and less soluble in the aqueous phase.

Figure 4-8 showed that for both composite volume samples and 1<sup>st</sup> pore volume as salt addition increased, so did the relative amount of Brij 97 that partitioned into the organic-rich phase. This result concurred with Kabalnov et al. (1995) who stated that increased salt would increase partitioning of a nonionic surfactant into an oil-rich phase. For the most part, the presence of Brij 97 increased as salt addition gradually increased. Total partitioning of the surfactant into the organic-rich phase did not occur in conjunction with the surfactant break-down after salt and temperature adjustments to the microemulsion system. Residual amounts of the surfactant in the separated aqueous phase were most likely part of the hydrophilic portion of the surfactant composition, and were presumably responsible for there not being a total partitioning of hydrophobic components into the organic-rich phase.

Comparing the different sets of samples showed that there was little discernible difference between the composite volume and 1<sup>st</sup> pore volume samples on the basis of surfactant partitioning into the organic-rich phase. Figure 4-8 displayed the relative concentration values of Brij 97 in the organic-rich phase as a function of salt addition

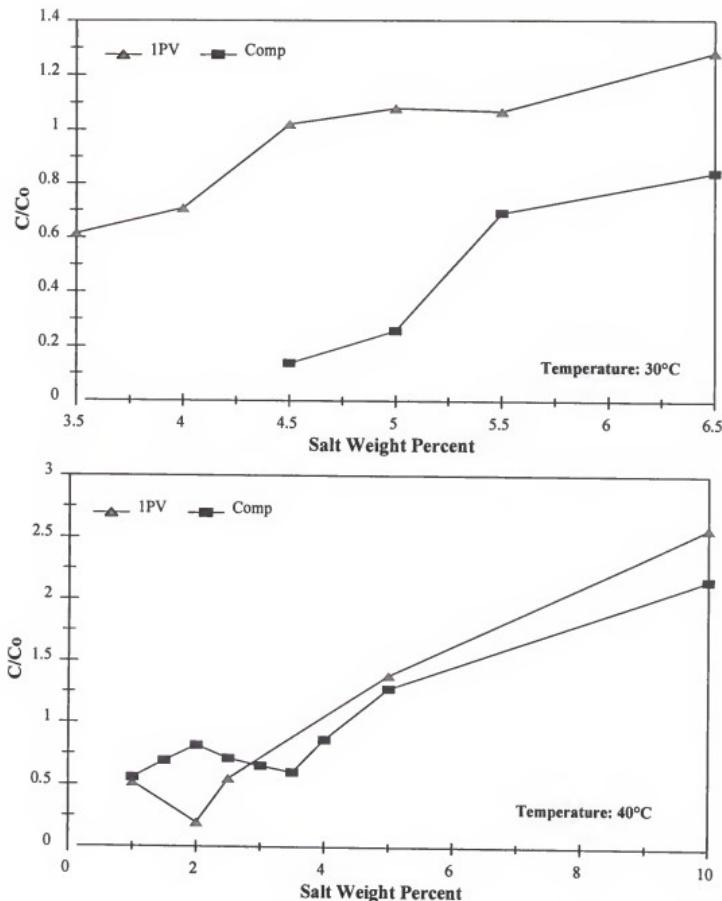


Figure 4-8 Relative concentrations of Brij 97 surfactant present in the separated organic phase of the composite volume and 1<sup>st</sup> pore volume samples as a function of the amount of salt added at various temperatures.

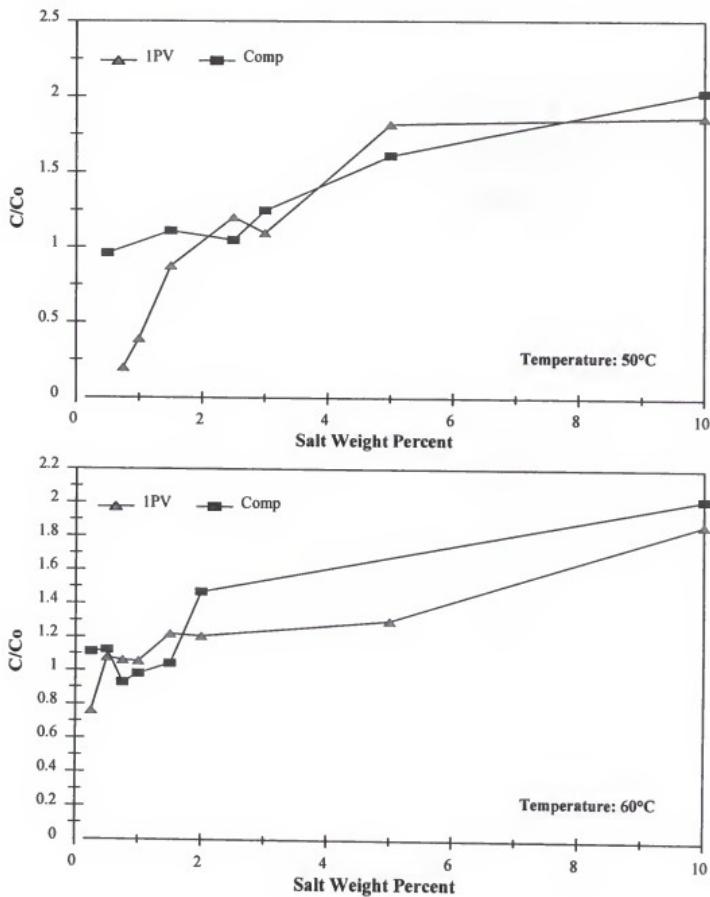


Figure 4-8 contd.

over a range of different temperatures. This figure showed, in general, that the partitioning of Brij 97 was relatively comparable for both composite volume and 1<sup>st</sup> pore volume samples. This was somewhat expected since the amount of surfactant, unlike NAPL encapsulated in the SPME effluent, was constant throughout the in-situ flushing experiment.

Comparing values at constant relative concentrations of Brij 97 in the organic-rich phase, a relationship between salt addition to ambient temperature was identified. For the 1<sup>st</sup> pore volume sample, to reach a Brij 97 relative concentration value of 1.25, salt concentrations of 6.5, 2.8, 1.8, and 0.9 were necessary for the temperature values of 30°C, 40°C, 50°C, and 60°C, respectively. For the composite volume sample, a Brij 97 relative concentration of 1.0 was reached by salt concentrations of 6.0, 4.5, 2.6, and 1.3 for the temperatures of 30°C, 40°C, 50°C, and 60°C, respectively. These results coincided with conclusions made by Kahlweit et al. (1990), by showing that as salt concentration increased in a nonionic surfactant system, the temperature necessary to cause equivalent partitioning of a surfactant into the organic-rich phase was reduced. So, although these values of the Brij 97 were just estimations of the surfactant concentration, the semi-quantitative method used allowed for general trends of partitioning into the immiscible phases to be approximated. This semi-quantitative method also provided results that validated the relationship between salt and temperature as mentioned in previous research.

COD

A chemical oxidation demand (COD) analysis was conducted on the resulting aqueous phase samples after immiscible phase separation. Figure 4-9 showed that there was little deviation between the COD values of the composite volume and 1<sup>st</sup> pore volume samples. Further, it was also found that for both the 1<sup>st</sup> pore volume and the composite volume samples that there was no discernible difference between the COD concentrations of the aqueous phases as a function of temperature. For 5 wt.% salt, COD concentrations for the 1<sup>st</sup> pore volume aqueous phase ranged from ~20,000 - 30,000 mg/L; and for the composite volume, it ranged from ~15,000 - 25,000 mg/L. No particular trend could be concluded from this COD data. However, for each temperature setting, as salt concentration increased, the COD concentration of the aqueous phase was found to generally decrease. At the temperature setting of 60°C, composite volume aqueous phase COD concentrations were found to be 28,000 mg/L; 22,000 mg/L; and 17,000 mg/L for salt concentrations of 1%, 2%, and 10%, respectively. Similar readings were also noted in the 1<sup>st</sup> pore volume set of samples on the basis of increasing salt concentrations. As temperatures increased, so did the similarity of the COD concentrations for the composite and 1<sup>st</sup> pore volume samples in the separated aqueous-rich phases.

As stated in previous chapters, approximately 99% of the COD load in the aqueous phase has been attributed to the presence of pentanol. Figures 4-10 and 4-11 present a distinct parallel between the amount of pentanol in the aqueous phase and the COD concentration in a system. For both composite volume and 1<sup>st</sup> pore volume sample

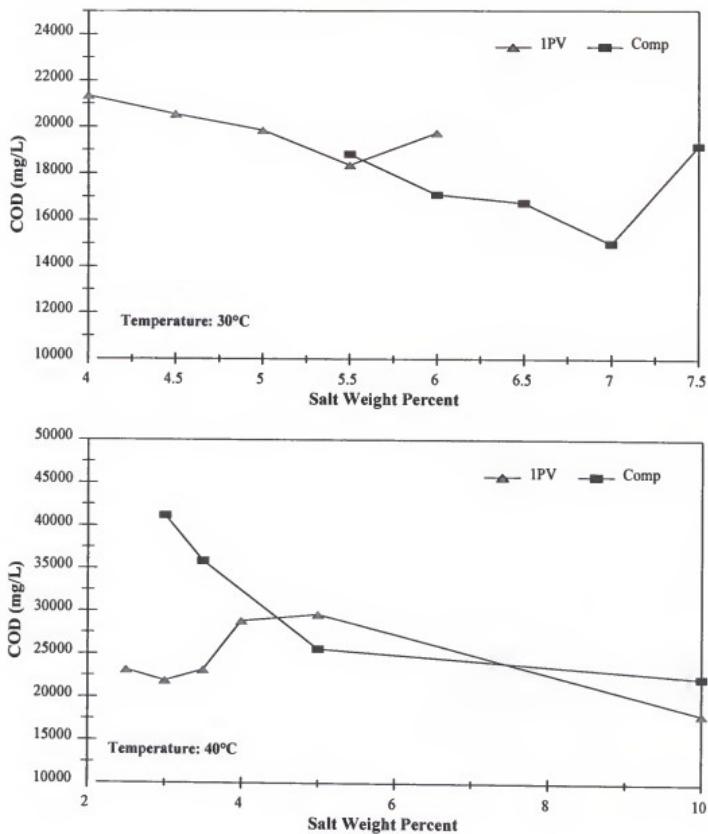


Figure 4-9 COD concentration present in the separated aqueous phase of the composite volume and 1<sup>st</sup> pore volume samples as a function of salt concentration for various temperatures.

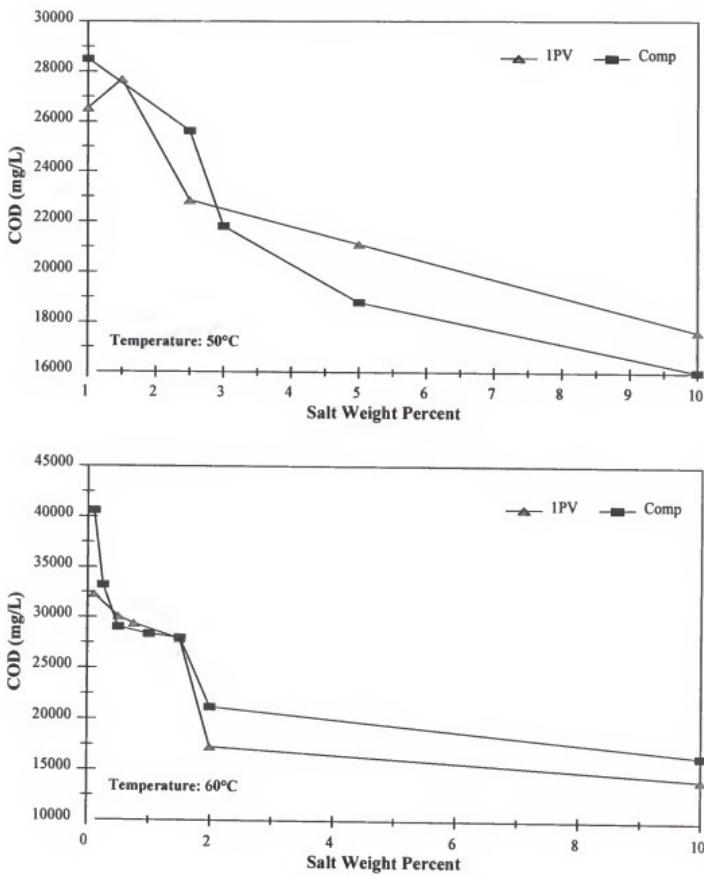


Figure 4-9 contd.

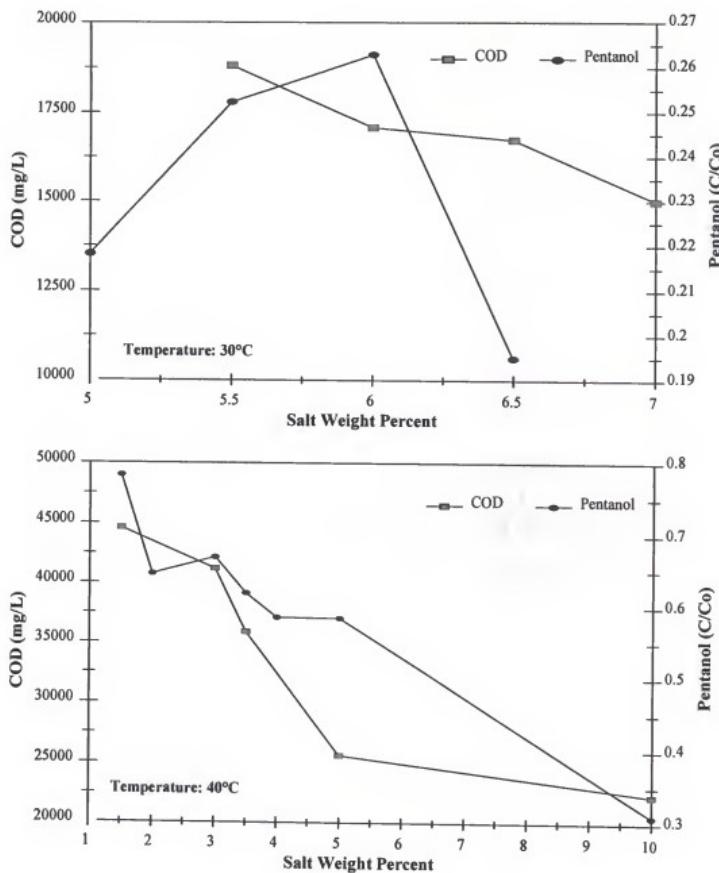


Figure 4-10 Comparison between the relative concentration of pentanol and the COD concentration in the separated aqueous phase of the composite volume samples as a function of salt concentration at various temperatures.

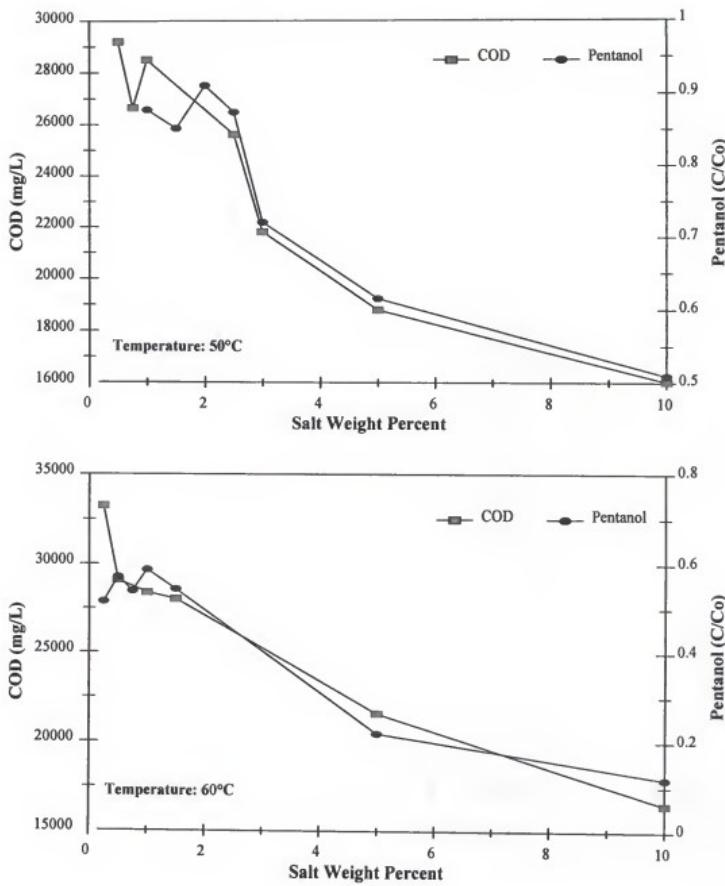


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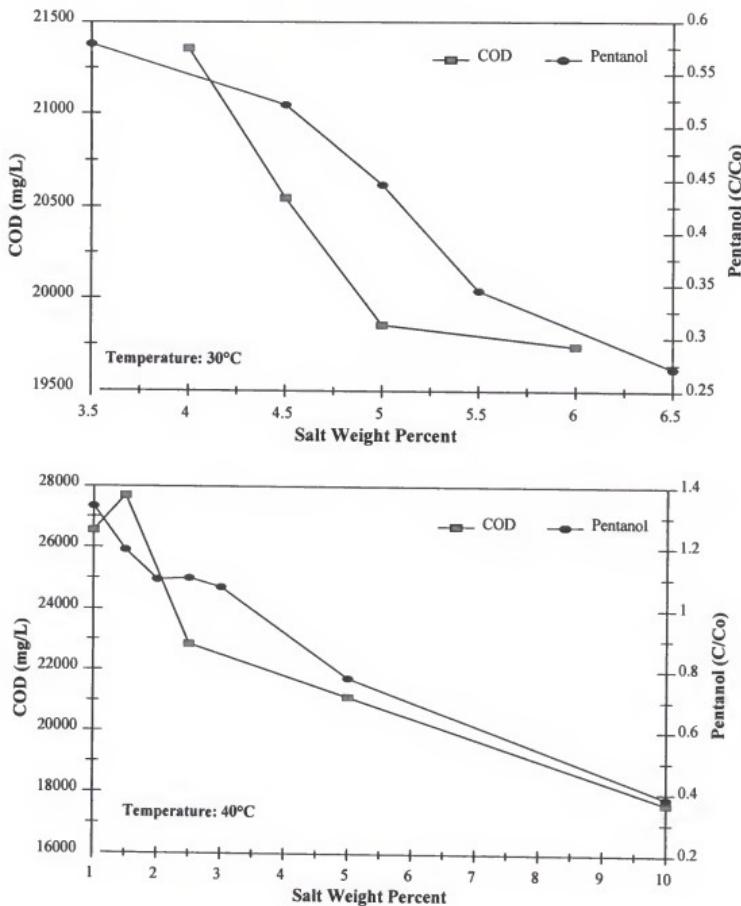


Figure 4-11 Comparison between the relative concentration of pentanol and the COD concentration in the separated aqueous phase of the 1<sup>st</sup> pore volume samples as a function of salt concentration at various temperatures.

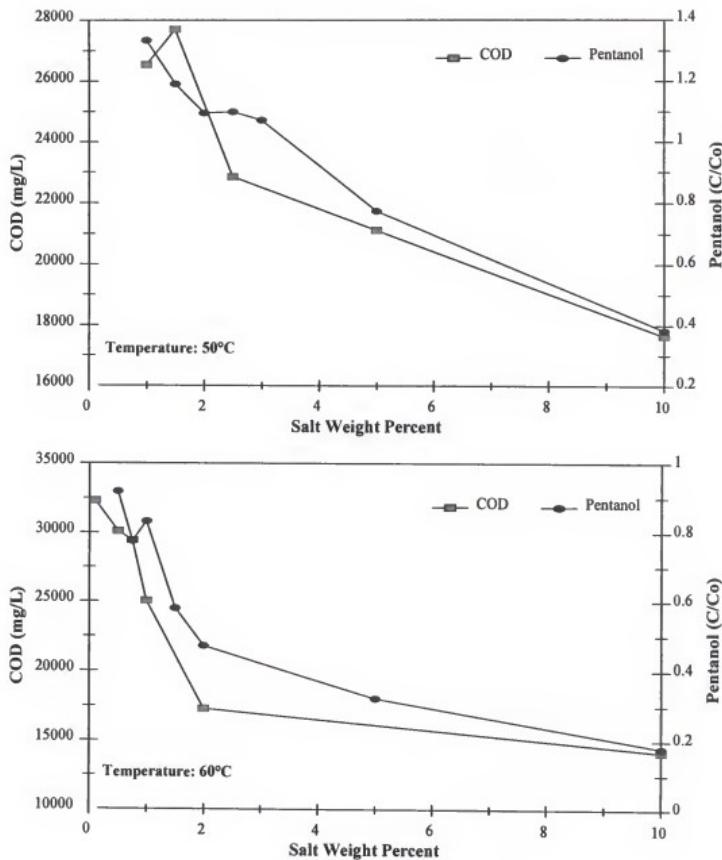


Figure 4-11 contd.

sets, it was seen that as salt weight percent increased, the COD concentration and pentanol concentration decreased. This relationship was also noticed irregardless of temperature setting. Since a majority of the COD load is related to pentanol presence in the aqueous phase, the removal of pentanol by methods such as air stripping should reduce COD levels of aqueous phase liquids sent to a wastewater treatment facility.

On the whole, the use of temperature and salt reduced the COD concentrations of the resulting aqueous phases significantly. The initial COD concentrations of the 1<sup>st</sup> pore volume and composite volume effluent SPME were 126,000 mg/L and 120,000 mg/L, respectively. For both the 1<sup>st</sup> pore volume and composite volume samples, approximately 90% of the COD concentration partitioned into the upper organic layer, leaving only a small fraction of the initial concentration remaining in the aqueous phase. This resulting COD concentration in the aqueous phase impacts the potential for treatment of this waste in certain industrial wastewater treatment plants. The lower the COD load, the easier and less expensive it is to treat, which improves the efficiency of the total remediation process.

Overall, it can be claimed that elevation of the ambient temperature of the SPME effluent increased the efficiency of separation by salt addition by reducing the amount of salt required to be added to the SPME effluent to achieve relatively high volumetric separation ratio values. The volumetric separation of the immiscible phases significantly increased with increasing temperatures at similar salt concentrations. Despite the improvement in the volumetric separation efficiency, mass of target analytes partitioning into the organic phase did not significantly increase, however, this is not seen as a

problem since generally >98% of the mass of these hydrophobic compounds partitioned into the separated organic phase. The COD load of the resulting aqueous phase following separation was seen to be significantly smaller than the effluent SPME. Therefore, in the cases of volume, mass, and COD concentrations, the use of salt at elevated temperatures proved to be an effective process for partitioning the NAPL contaminant in the effluent SPME into the upper organic phase away from the lower aqueous phase.

### Conclusions

The purpose for this experiment was to study a potential intermediate treatment process that could possibly reduce the amount of waste that would require expensive treatment by incineration by employing phase separation. This intermediate treatment process consisted of the addition of various amounts of salt at elevated temperatures to an effluent single phase microemulsion (SPME) waste produced by a subsurface remediation of a contaminated soil. The addition of salt and temperature were found to produce significant immiscible phase separation of the initial effluent microemulsion.

It was determined that salt at elevated temperatures effectively separated the SPME effluent into two immiscible phases for further treatment and/or disposal. In relation to this, it was also determined that for increasing temperatures, lower amounts of salt were required to produce similar levels of volumetric phase separation. Additionally, at specific temperature levels, the composite volume samples generally required less salt to achieve similar volumetric separation when compared to the 1<sup>st</sup> pore volume samples. The ratio of aqueous-rich separated phase volume to initial pre-treated SPME effluent

volume was also seen to increase with increasing addition of salt at every temperature level. The most efficient separation for the elevated temperatures indicated that through this intermediate treatment method, the volumes of NAPL-dominated waste have been shown to be reduced by over 95%.

Generally, the mass of all of the hydrophobic components, especially those that made up the surfactant and NAPL contamination, were shown to end up in the compact volume of the organic-rich phase. Percentages of the mass of these target analytes in the organic-rich phase were generally constant and usually >98%. The percentage of pentanol mass partitioning into the organic-rich phase was not as high as the target analytes, but was seen to increase with increasing weight percent of salt added. Data for pentanol also indicated that as ambient temperature increased, less pentanol on a percent mass basis was found to partition into the organic-rich phase.

An increase in salt addition at constant temperature values was shown to increase the relative concentrations of the NAPL target analytes and pentanol in the organic-rich phase of both composite volume and 1<sup>st</sup> pore volume samples. However, as temperature was seen to increase at constant salt concentrations, the composite volume samples showed an increase in relative concentrations of target analytes, while for the 1<sup>st</sup> pore volume samples, these values remained comparatively constant.

A semi-quantitative method allowed for an estimation of surfactant concentration in both separated phases. This estimation based upon GC analysis showed that individually increasing the temperature or salt concentration led to the concentration and partitioning of the Brij 97 nonionic surfactant into the organic-rich phase and away from

the aqueous phase. Further, the partitioning of Brij 97 was also found to be relatively comparable for both composite volume and 1<sup>st</sup> pore volume samples.

There was no discernible difference between the COD concentrations of the separated aqueous phases as a function of temperature or as a function of when the sample was taken. However, for each temperature, as salt concentration increased, the COD concentration of the aqueous phase generally decreased. Additionally, a distinct parallel was found between the COD concentration of the aqueous-rich phase and the concentration of pentanol remaining in that phase. For both the 1<sup>st</sup> pore volume and composite volume samples, approximately 90% of the COD concentration partitioned into the upper organic layer after salt and temperature separation.

In summary, it can be stated that the increase in the ambient temperature of the SPME effluent increased the efficiency of separation by salt addition. In the cases of volumetric, mass, and COD concentration analysis, the use of salt at elevated temperatures proved to be an effective process for partitioning the NAPL contaminant in the effluent SPME into the upper organic phase away from the lower aqueous phase. Reducing the volume of waste containing NAPL may allow for a reduction in the expense allocated for treatment of residual waste, thereby, proving to be economically beneficial to the overall remediation project.

## CHAPTER 5

### IRON TREATMENT OF CHLORINATED WASTE SOLUTIONS

#### Introduction

Remediation of ground water contaminated by halogenated organic compounds is a significant priority in the environmental field. Furthermore, with the limitations of conventional pump-and-treat technologies documented (Augustijn et al., 1994; Keely, 1996; Fennelly and Roberts, 1998), the addition of chemical additives as cosolvents has achieved recent success in the removal of halogenated organics from subsurface environments (Palmer and Fish, 1996; Rao et al., 1997). Special concern in this area has been directed at chlorinated organic compounds because of their widespread use in industrial, military, and commercial applications. Their detrimental effects to both the environment and human health are well documented (Hooker and Klabunde, 1994; Butler and Barker, 1996; Hua and Hoffman, 1996). Although, the use of zero-valent metals, especially iron (Sweeny, 1981; Gillham and O'Hannigan, 1994; Helland et al., 1995; Muftikian et al., 1995; Johnson et al., 1996; Korte et al., 1997), has recently produced success in treatment of chlorinated organic solutions (Wilson, 1995; Agrawal and Tratnyek, 1996; Tratnyek et al., 1997; Powell and Puls, 1997), research into the effects of cosolvents on these applications has not been thoroughly investigated. This information would be useful in designing systems utilizing iron for treatment of chlorinated pollutants.

removed by innovative cosolvent flushing procedures.

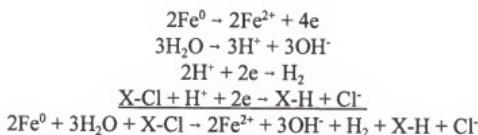
The purpose of this research was to evaluate the effectiveness of zero-valent iron ( $\text{Fe}^0$ ) in treating a solution which contained perchloroethylene (PCE), and how addition of cosolvent (ethanol) to this solution would affect these results. Modifications to the zero-valent iron, including acid treatment and nickel plating, were also investigated in treating PCE solution containing the different cosolvent fractions. This should provide information about the effectiveness of different forms of iron for treating PCE in the presence of different cosolvent fractions used in removing it from the subsurface. This information could be used in designing ex-situ treatment systems for chlorinated organic waste generated from cosolvent flushing at DNAPL sites.

### Background

The use of buried walls of elemental iron in dechlorination is an example of passive in-situ treatment. Passive in-situ treatment system involves no external energy or chemical input, no extraction or forced fluid circulation, and no maintenance or replacement of reactive materials (Cherry et al., 1996). Gillham and O'Hannessin (1994) describe laboratory and field prototype trials of a solid-phase treatment material ( $\text{Fe}^0$ , elemental iron fillings) for in-situ destruction of chlorinated solutions. Iron offers good prospects to achieve passive treatment of solvent plumes over long periods of time (Agrawal and Tratnyek, 1996; Powell and Puls, 1997). Other applications of iron treatment for chlorinated solvents are also provided in the literature (Grittini et al., 1995; Appleton, 1996; Wang and Zhang, 1997; Charlet et al., 1998; Johnson et al., 1998).

### Degradation of Chlorinated Organics

The degradation of the chlorinated organics is an abiotic process and there is generally a simultaneous occurrence of two reactions in dechlorination using elemental iron, oxidation of iron by water and reductive dechlorination (with the Fe<sup>0</sup> serving as the source of electrons). Gillham and O'Hannesin (1994), Helland et al. (1995), and Muftikian et al. (1995) reported that reactions could be depicted by the following equations:



Gillham (1996) stated that in the presence of chlorine, the carbon in chlorinated compounds tend to be in the oxidized state and thus the compounds tend to be thermodynamically unstable in a reducing environment. This highly reducing environment is provided by the zero-valent iron metal, and other metallic combinations. Gillham and O'Hannesin (1994) had previously concluded that the rate of degradation declined with decreasing degree dechlorination.

Matheson and Tratnyek (1994) described a general model for surface reactions as consisting of the five following steps: (i) mass transport of the reactant to the Fe<sup>0</sup> surface from the bulk solution; (ii) adsorption of the reactant to the surface; (iii) chemical reaction at the surface; (iv) desorption of the product(s); and (v) mass transport of the product(s) to the bulk solution. Matheson and Tratnyek (1994) and Burris et al. (1995) went on to report that acid washing of the iron provided faster dechlorination rates. This

was stated to be a result of the acid dissolving the surface layer of the iron grains which may contain unreactive oxide or organic coatings. The clean, reduced metal surface in conjunction with greater surface area due to corrosion pits are credited with greater reactivity on the acid washed iron. Also, there was no evidence of residual acidity, so the observed dehalogenation rate could not be attributed to the effect of pH (Matheson and Tratnyek, 1994).

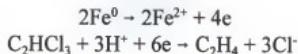
The iron degradation reactions with respect to chlorinated organics have been reported to be pseudo first-order by several researchers (Matheson and Tratnyek, 1994; Gillham and O'Hannesin, 1994; Helland et al., 1995; Orth and Gillham, 1996). Only Burris et al. (1995) concluded that reduction of PCE and TCE on zero-valent iron is not a pseudo-first order reaction, but stated that this is a complex reaction involving a series of interconnected processes (nonreactive sites, competition between sorbing chemicals). The contaminant mass in the aqueous phase appears to be the portion of the total mass that is available for reduction. Burris et al. (1995) went on to state that in accounting for the sorption to nonreactive sites, the loss of PCE and TCE was shown to be a first-order process. However, when not including a site balance for chemical adsorption, as in Burris et al. (1995), the pseudo first-order reaction rate has been consistently shown to best represent the reaction process in the aforementioned literature.

Reductive dechlorination can occur anaerobically under strongly reducing conditions, especially in the presence of galvanized steel, stainless steel, aluminum, and iron. Due to its low cost and nontoxicity, iron was proposed for in-situ remediation of contaminated groundwaters (Gillham and O'Hannesin, 1994; Matheson and Tratnyek,

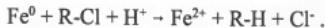
1994). Other metals especially zinc, tin, nickel, and palladium have been reported to transform halogenated organic carbons more rapidly than iron (Grittini et al., 1995; Gillham, 1996; Liang et al., 1997). These metals, when combined with iron to form bimetallic surfaces, act as a catalyst to accelerate the disassociation of the chlorinated hydrocarbons, by preventing formation of iron oxides and by their own highly reducing nature (Wang and Zhang, 1997). Iron is still used as the basic substrate for possible industrial uses due to its marginal effectiveness and, more importantly, its low cost for the large quantities that would be required at a field site (Gillham and O'Hannesin, 1994).

The degradation of PCE has received limited exposure in the literature, especially in the presence of iron. However, Gillham and O'Hannesin (1994) reported degradation of PCE with zero-valent iron in batch tests with initial concentration levels around 2 ppm. Gillham and O'Hannesin (1994) also stated that no other degradation products were detected and this led to the suggestion that with  $\text{Fe}^0$  reductive dechlorination was a simple process with  $\text{Fe}^0$  serving as the electron source. Gillham and O'Hannesin (1994) also mentioned that the corrosion of iron by water continues independently of the organic degradation reaction, so they were able to conclude that there is no relationship between iron concentration and organic degradation. Further, their study showed that iron and zinc (galvanized metal) were found to give similar rates of degradation, followed by aluminum, and with brass and copper giving much lower rates.

The chlorinated alkene, TCE, received moderate attention in the literature. Matheson and Tratnyek (1994) predicted that degradation of TCE would include the following equations:



and reported significant degradation of TCE, which was not specifically explored in their work. However, Orth and Gillham (1996) and Liang et al. (1997) reported experimental success in dechlorination of TCE by iron metal. Another similar chlorinated compound, carbon tetrachloride ( $\text{CCl}_4$ ) was also seen to degrade significantly in the presence of iron (Helland et al., 1995; Johnson et al., 1996). Helland et al. (1995) reportedly described hydrogenolysis as the process by which chlorinated pollutants are reductively dechlorinated to less persistent and often less toxic forms. Helland et al. (1995) stated that hydrogenolysis involves the reduction of a pollutant with electrons from an external source ( $\text{Fe}^0$ ). The use of  $\text{Fe}^0$  in the dechlorination reduction of PCE falls into this category. Similar to other literature, Helland et al. (1995) described the surface controlled hydrogenolysis of alkyl chlorides ( $\text{R-Cl}$ ) by  $\text{Fe}^0$  with the following equation:



#### By-Product Formation

Some researchers agree that a comprehensive study of degradation by products of most chlorinated organics has yet to be performed (Gillham and O'Hannesin, 1994; Liang et al., 1997; Charlet et al., 1998). Further, many admit that there is relatively little known about the transformation pathways of dechlorination (Matheson and Tratnyek, 1994; Gillham and O'Hannesin, 1994; Burris et al., 1995; Grittini et al., 1995). However, as previously stated, it is generally accepted that the reaction is electrochemical in nature, involving oxidation of the iron and reductive chlorination of the organic compounds, and

there is production of hydrogen gas. Additionally, the degradation is thought of as a simple dechlorination process, with Fe<sup>0</sup> serving as the source of electrons (Matheson and Tratnyek, 1994; Helland et al., 1995; Muftikian et al., 1995; Orth and Gillham, 1996).

Orth and Gillham (1996) showed that ethene (C<sub>2</sub>H<sub>4</sub>) and ethane (C<sub>2</sub>H<sub>6</sub>) in a ratio of about 2:1 constitute over 80% of the mass (in terms of equivalent TCE) of the hydrocarbons that were identified in the dechlorination of TCE (trichloroethylene) with Fe<sup>0</sup>. However, there were small amounts of chlorinated products found after degradation which included: *cis*-1,2-dichloroethylene (DCE), *trans*-1,2-DCE, 1,1-DCE, and vinyl chloride (VC). But, the sum of these chlorinated products represented about 3-3.5% of the TCE that was degraded. Tratnyek et al. (1997) admitted that in cases, such as dechlorination with Fe<sup>0</sup>, contaminant degradation leads to several possible products, and that there is little data about how the sequential degradation pathways behave under operational conditions. Burris et al. (1995) went on to concur that the mechanism for reduction of chlorinated solvents by metallic iron is poorly understood, but that a heterogeneous reaction is indicated by a strong dependence of reaction rate on iron surface area and the lack of reaction when water is removed from the iron surfaces. Some of the possible degradation pathways of PCE (Figure 5-1) and their rate constants (Table 5-1) were reported in 1996 by Burris et al. and in 1998 by Arnold and Roberts, but there has been no reproducible kinetic data that would aid in pathway probability calculations.

There has been little, if any, literature to date that explores the effect of cosolvents on iron degradation of chlorinated organics. Perhaps this is due to the belief that sorption of contaminants onto the iron is the controlling factor in the degradation of the

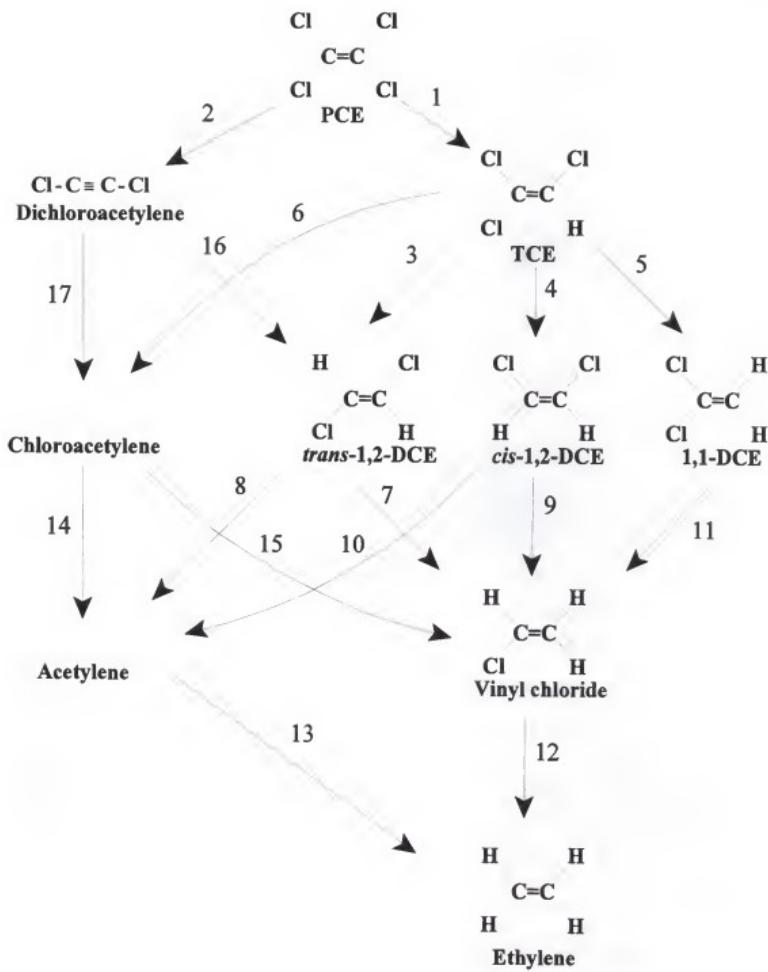


Figure 5-1 Proposed pathways for PCE degradation (Arnold and Roberts, 1998)

Table 5-1. Surface area-normalized rate constants for chlorinated ethylenes and their reaction products (Arnold and Roberts, 1998).

Rxn #	Reaction	$k_{SA}$ ( $L\ m^{-2}\ hr^{-1}$ )
1	PCE → TCE	0.3
2	PCE → Dichloroacetylene	$4.5 * 10^{-2}$
3	TCE → <i>trans</i> -DCE	$1.5 * 10^{-3}$
4	TCE → <i>cis</i> -DCE	$6.0 * 10^{-4}$
5	TCE → 1,1-DCE	$6.8 * 10^{-5}$
6	TCE → Chloroacetylene	$9.4 * 10^{-4}$
7	<i>trans</i> -DCE → VC	$6.4 * 10^{-7}$
8	<i>trans</i> -DCE → Acetylene	$1.3 * 10^{-5}$
9	<i>cis</i> -DCE → VC	$5.2 * 10^{-7}$
10	<i>cis</i> -DCE → Acetylene	$3.0 * 10^{-6}$
11	1,1-DCE → VC	$4.1 * 10^{-5}$
12	VC → Ethylene	$1.0 * 10^{-4}$
13	Acetylene → Ethylene	$5.0 * 10^{-4}$
14	Chloroacetylene → Acetylene	6.5
15	Chloroacetylene → VC	0.5
16	Dichloroacetylene → <i>trans</i> -DCE	20.6
17	Dichloroacetylene → Chloroacetylene	4.4

chlorinated organic compounds. In this vein, Burris et al. (1995) did conclude that the sorption of PCE and TCE to zero-valent iron was nonlinear and described the phenomenon by a generalized Langmuir sorption isotherm equation. That research did not explore the effects of chlorinated compounds sorption with respect to cosolvent influence. The major effect of cosolvents is to improve the solubility of non aqueous phase liquids (NAPLs), like chlorinated compounds, into aqueous systems, thereby decreasing their ability to adsorb on solid matrices. Therefore, increasing cosolvent fraction is expected to decrease degradation of PCE simply by reducing the ability of the compound to adsorb to the iron surface.

#### Materials and Methods

Individual batch reactor systems analyzed over a two week time period, were used to evaluate the degradation kinetics in aqueous solutions containing PCE at different concentrations and at various (ethanol) cosolvent fractions. The iron degradation of PCE at initial concentration levels of ~ 2 µg/ml (ppm) and ~55 µg/ml were investigated at ethanol fractions of 0%, 10%, 30%, and 50%. This would show if degradation was concentration-dependent, and how various cosolvent contents would affect this process over a two-week period.

Each batch reaction took place in a 5-mL glass vial fitted with a teflon-lined septa screw-top cap. The vial was initially weighed empty, then a mass of iron (approximately 1.25 g) was added to the 5-mL vial and weighed again. The vials were then filled to the top with solutions containing PCE at various ethanol fractions, allowing no headspace,

and re-weighed. This generally provided a 4:1 volume/mass ratio, which was used by Gillham and O'Hannessin (1994) and Muftikian et al. (1995) for batch tests in their research. The vials were then placed on a rotator (15 rev/min), and samples were taken off the rotator at the desired sampling times. Aqueous-phase samples were transferred to 0.5-ml vial inserts for GC analysis. The remaining aqueous volume above the iron was removed and the vial re-weighed.

#### Desorption

To determine the mass of the PCE sorbed to the iron, the PCE was desorbed from the iron and analyzed separately. For the 55 ppm PCE concentration samples, PCE was desorbed by adding methanol (MeOH) to the vial with the remaining iron. After equilibrium was reached, the sample representing the sorbed phase concentration was transferred to a 0.5 mL vial insert for analysis. This procedure for both aqueous and sorbed phase sampling was followed for each experiment, except for the 2 ppm PCE analysis. For low-concentration analysis (<2 ppm), hexane extractions were conducted because the samples were being analyzed by GC/ECD (gas chromatograph/electron capture detector). Both the aqueous and sorbed phase 2 ppm samples were extracted with a 1:1 ratio of hexane.

Except for the <2 ppm samples, analysis was conducted on a Shimadzu-10A High Performance Liquid Chromatograph (HPLC) System fitted with a Supelco PAH-C18 Column. The system was equipped with a UV-VIS Detector set at a wavelength of 230 nm. The mobile phase was run at a velocity of 2 mL/min, and contained 65% methanol and 35% HPLC water.

For the hexane extracted <2 ppm samples, analysis was conducted on a Shimadzu GC-17A System which included a J&W Scientific DB-624 Column (30m x 0.53mm x 3 $\mu$ m). The GC was equipped with a  $^{63}\text{Ni}$  electron capture detector (ECD), and nitrogen acted as the carrier gas.

#### Pretreatment of Iron Filings

Three types of iron were evaluated in this research. Iron filings purchased from Fisher Scientific, nickel-plated iron, and pretreated iron. The nickel-plated iron filings provided by Stephanie O'Hannesin (Environmental Technologies, Inc., Guelph, Ontario) were industrially produced. Pretreatment of the zero-valent iron filings were conducted to remove possible impurities that may hinder surface catalysis. Matheson and Tratnyek (1994) noted that increasing the clean surface of iron greatly increases dehalogenation. Acid pretreatment of the filings was done similar to the methods reported by Matheson and Tratnyek (1994), Muftikian et al. (1995) and Liang et al. (1997).

A quantity of iron filings were placed in a beaker and 1N HCl solution was added to cover the filings completely. A pasteur pipette was used to mix the filings and acid solution to ensure full contact of the filings with the solution. Approximately 30 minutes of equilibration time with occasional mixing was employed for this step of the iron treatment. Once equilibrium was reached, the acidic solution was decanted and degassed deionized (DI) water was added to the filings, mixed thoroughly, and then decanted. The filings were then rinsed with degassed DI water several times in this same manner.

The iron filings with a small amount of DI water were transferred to an Erlenmeyer flask with an off-gas nozzle. The flask was connected through a rubber

stopper cap to a N<sub>2</sub> tank, and placed on a hot plate. This was done to dry the iron filings without oxygen to prevent the production of oxides on the iron surface. Helland et al. (1995) also reported that oxygen could also inhibit dechlorination by binding to the iron surface and reducing the availability of reactive surface sites. Nitrogen was passed across the heated filings at a low flow rate until the filings were completely dry. The flask was then sealed and stored in a dessicator until the filings were to be used. The treated filings had a black color, while the untreated filings were gray in color.

### Results and Discussion

Experimental batch tests measuring degradation of PCE in the presence of Fe<sup>0</sup> were conducted for both relatively high (~55 ppm) and low (>2 ppm) PCE concentrations, and, furthermore, for the different forms of modified zero-valent iron. Based on effluent concentration estimates given by Tim McHale of ManTech Environmental Research Services Corporation, the concentration of PCE in a total effluent flush, including tracer studies, was found to be approximately 125 ppm. However, this was not taking to account the groundwater flushed through the contaminated zone before and after the flushing experiment was conducted. This additional water treated in the total waste volume would conceivably reduce the concentration of PCE in the total waste effluent to near 55 ppm, which was the concentration that was used in this research.

The different zero-valent iron types included acid-treated iron (TreatFe) and nickel-plated iron (NiFe). These experiments provided the opportunity to evaluate the

effectiveness of PCE degradation as a function of concentration and iron modification.

Additionally, various cosolvent (ethanol) fractions in the solutions containing PCE were evaluated as well. This provided data on the relationship between adsorption and degradation, as well as how cosolvent remediation fluids might react when treated with zero-valent iron.

#### Degradation of PCE

Batch test results showed that PCE degraded in the presence of  $\text{Fe}^0$ . These degradation reactions were found to be pseudo first-order when  $\ln(C_w)$  was plotted versus time (Figures 5-2 through 5-5). This pseudo first-order relationship was also observed by previous researchers (Matheson and Tratnyek, 1994; Gillham and O'Hannessin, 1994; Helland et al., 1995; Orth and Gillham, 1996). As the natural log of the PCE concentrations in the batch reactor vials ( $C_w$ ) were plotted as a function of time, the slope of these plots were generally linear and known as the pseudo first-order PCE loss or disappearance rates in the batch reactor vials,  $K'$  ( $\text{hr}^{-1}$ ), and are displayed in Table 5-2. This slope was also found to be:

$$K' = \frac{-k a_s}{V/a_s + K_i}$$

where  $a_s$  denotes the surface area of the iron ( $\text{cm}^2$ );  $V$  represents the solution volume (ml,  $\text{cm}^3$ );  $k$  represents the PCE degradation rate that took place on the iron surface ( $\text{cm}^{-1} \text{hr}^{-1}$ ); and  $K_i$  was known as the concentration-independent adsorption coefficient ( $\text{cm}^3/\text{cm}^2$ ) described by Kim et al. (1998).

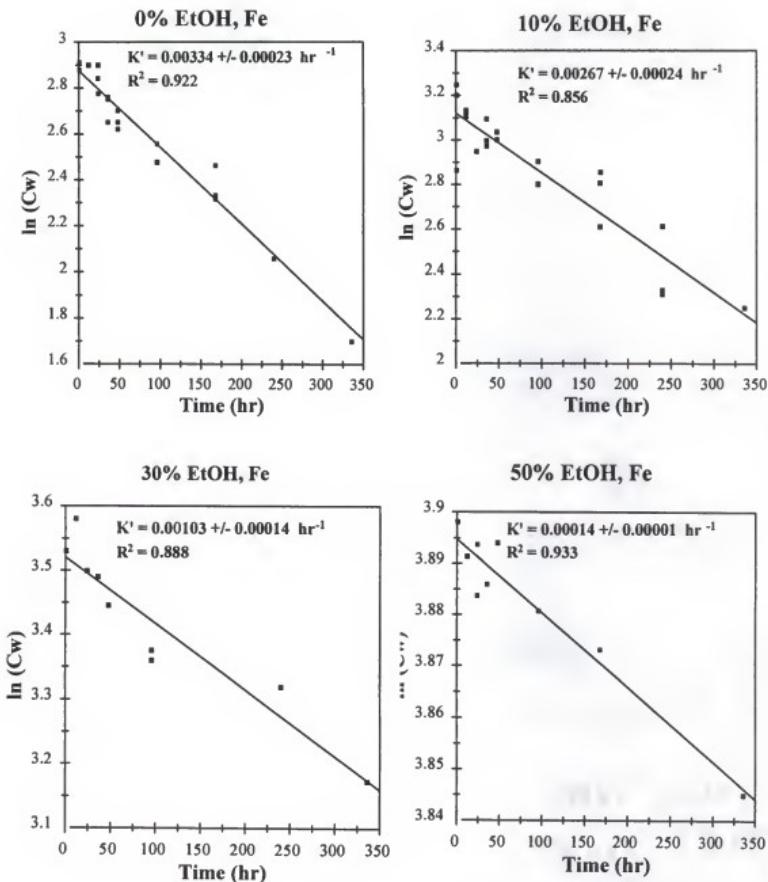


Figure 5-2 Pseudo first-order degradation plots of PCE in the presence of untreated zero-valent iron as a function of different ethanol fractions in solution

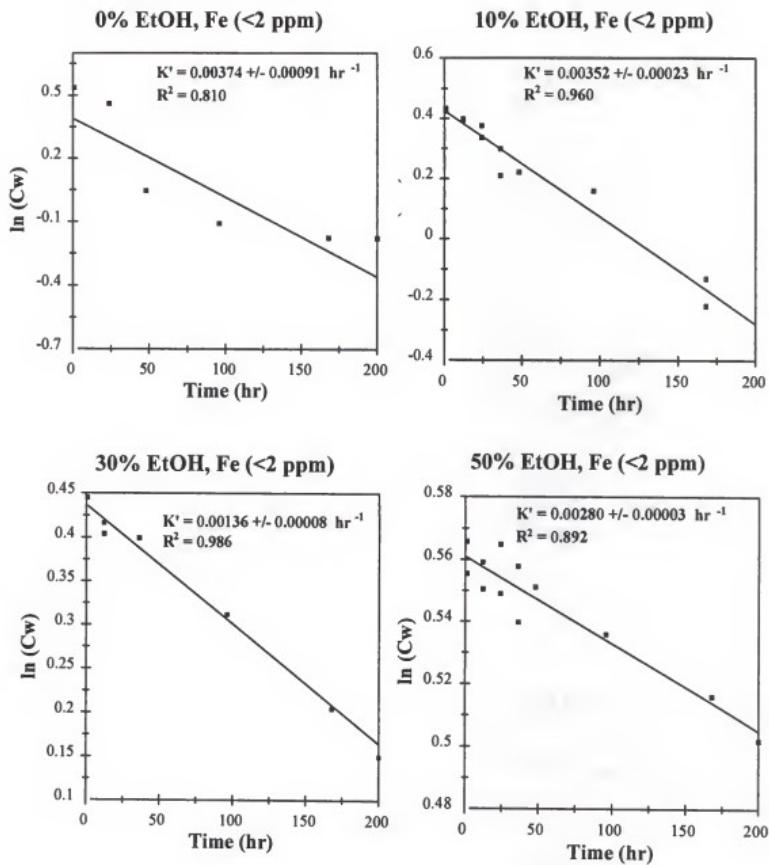


Figure 5-3 Pseudo first-order degradation plots of PCE in the presence of untreated zero-valent iron (initial concentration <2 ppm) as a function of different ethanol fractions in solution

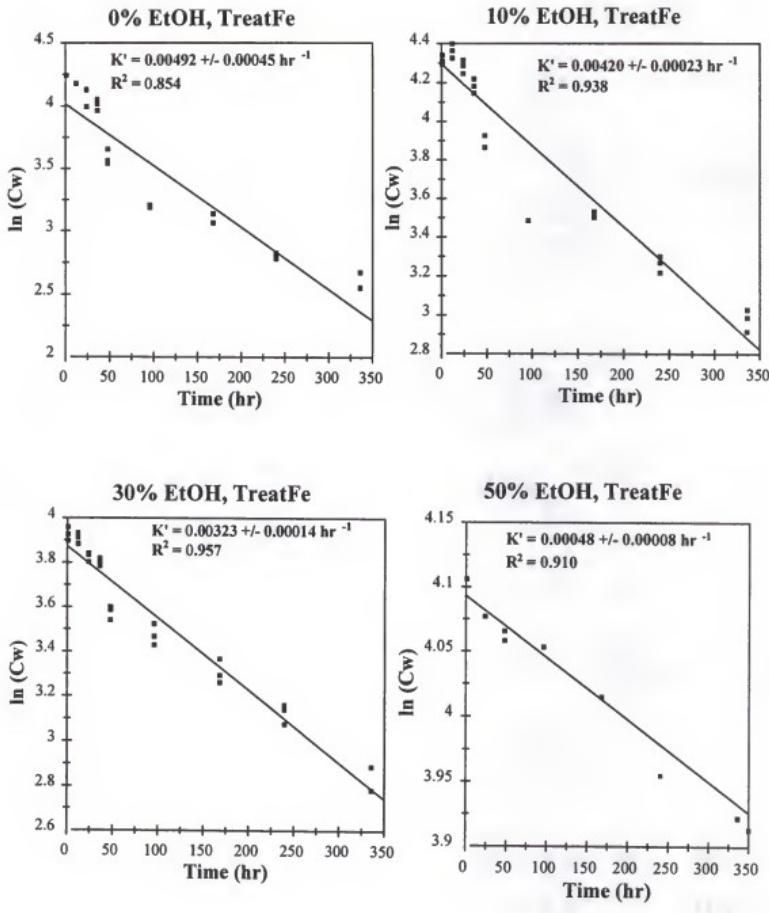


Figure 5-4 Pseudo first-order degradation plots of PCE in the presence of acid treated iron as a function of different ethanol fractions in solution

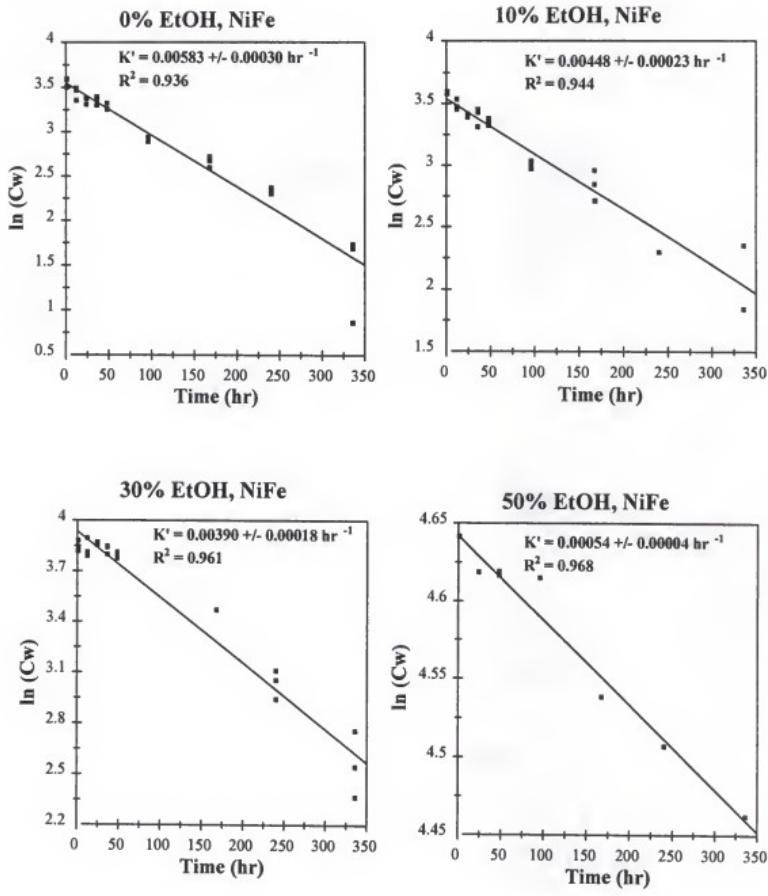


Figure 5-5 Pseudo first-order degradation plots of PCE in the presence of nickel-plated iron as a function of different ethanol fractions in solution

Table 5-2. Pseudo first-order rate constants for PCE disappearance in cosolvent solutions in contact with various types of modified iron surfaces.

		Degradation Rate Constant, $K' \times 10^3$ (hr <sup>-1</sup> )			
Type of Iron ( $C_0 \approx 55$ µg/ml PCE)	Ethanol				
	0 %	10%	30%	50%	
Nickel Iron	5.83	4.48	3.90	0.54	
Treated Iron	4.92	4.20	3.23	0.47	
Untreated Iron	3.34	2.67	1.03	0.14	
Untreated Iron (<2 µg/ml)	3.74	3.52	1.36	0.29	

Table 5-3. Half-lives of solutions which contain PCE in contact with various types of modified iron, ethanol fractions, and initial concentrations.

		Half-life, $t_{1/2} \times 10^2$ (hr)			
Type of Iron ( $C_0 \approx 55$ µg/ml PCE)	Ethanol				
	0 %	10%	30%	50%	
Nickel Iron	1.19	1.55	1.78	12.77	
Treated Iron	1.41	1.65	2.14	14.52	
Untreated Iron	2.08	2.59	6.72	47.97	
Untreated Iron (<2 µg/ml)	1.85	1.97	5.09	24.28	

The slope of PCE disappearance was determined by conducting a PCE mass balance including the aqueous and adsorbed phases based on the equation:

$$\frac{dM_T}{dt} = \frac{d(V_w C_w + a_s \Gamma_s)}{dt} = -k a_s \Gamma_s$$

where  $M_T$  represents the total mass of PCE ( $\mu\text{g}$ ) degraded over time  $t$  (hr);  $V_w$  represents the volume of the aqueous phase (ml);  $C_w$  stands for the PCE concentration in the aqueous phase ( $\mu\text{g}/\text{ml}$ );  $\Gamma_s$  symbolizes the surface excess quantity of PCE on the iron ( $\mu\text{g}/\text{cm}^2$ ). It was expected that the change in mass over time ( $dM_T/dt$ ) was nearly equal to  $-k a_s \Gamma_s$  due to the assumption that degradation on the solid phase would dominate when compared to that in the aqueous phase. Kim et al. (1998) further stated that:

$$\Gamma_s = K_i C_w$$

so, by substituting the value for  $\Gamma_s$  into the mass balance equation seen earlier and integrating, the resulting equation was linear with respect to  $\ln(C_w)$  versus time with a  $-K'$  slope. Half-lives for loss of PCE were listed in Table 5-3. The degradation rates of PCE explicitly on the iron surfaces,  $k$ , were also calculated and displayed in Table 5-4. Later, the degradation that occurs in the system was shown to be a function of the mass present on the iron surface.

Half-lives of PCE loss calculated from the pseudo first-order rate constants are listed on Table 5-3. The half-life of PCE in contact with untreated iron was approximately 208 hr (8.7 days), which was an order of magnitude higher than the value of 20 hr reported by Gillham and O'Hannessin (1994). However, this half-life value was

Table 5-4. First-order surface degradation rate constants for PCE on various types of modified iron surfaces in cosolvent solutions.

Type of Iron (C <sub>0</sub> ≈ 55 µg/ml PCE)	Degradation Rate Constant, k*10 <sup>11</sup> (cm <sup>-1</sup> hr <sup>-1</sup> )			
	0 %	10%	30%	50%
Nickel Iron	6.45	4.99	4.15	0.56
Treated Iron	208.27	172.46	132.40	19.49
Untreated Iron	136.64	109.20	41.78	5.82
Untreated Iron (<2 µg/ml)	153.34	143.65	55.11	11.50

Table 5-5. Partition coefficients (K<sub>d</sub>) for PCE in contact with different types of modified iron and various ethanol fractions.

Type of Iron	Partition Coefficient, K <sub>d</sub> (ml/g)		
	10%	30%	50%
Nickel Iron	0.613	0.405	0.265
Treated Iron	0.365	0.313	0.260
Untreated Iron	0.295	0.263	0.235

comparable with the value of 13.9 days reported by Wilson (1995). Although the mass to volume ratio was the same for the Gillham and O'Hannessin (1994) research, the actual masses and volumes were not the same as used in this research. Also, Gillham and O'Hannessin (1994) rotated their batch reactors at 2 revs/min, while for this research, the batch reactors were rotated at 15 revs/min. The faster rotator velocity used in this research probably led to reduced adsorption of PCE on the iron surfaces, and thus, the increased half-lives compared to those reported by Gillham and O'Hannessin (1994).

In comparing the different concentration levels, the degradation of the higher concentration of PCE (~ 55 ppm) with untreated iron occurred more slowly than that of the lower (>2 ppm) PCE concentration (Tables 5-2 and 5-3). This seemed to indicate that the PCE molecules competed for a limited number of sorption sites on the iron surface. This competition resulted in the fact that the solution with fewer PCE molecules (>2 ppm) could find a greater number of uninhabited sorption sites faster, and, therefore, be degraded at a faster rate than the solution with more PCE molecules present and the same relative number of sorption sites. This relationship was found to be consistent throughout the PCE solutions containing various ethanol fractions (Figures 5-2 and 5-3).

Experiments using the modified iron (acid treated and nickel-plated) were also shown to yield pseudo first-order degradation reaction rates (Figures 5-4 and 5-5). Comparing the different types of iron employed in this research showed that the NiFe was the most effective, followed by TreatFe, and, finally, the untreated Fe<sup>0</sup> was the least effective in degrading the PCE at 55 ppm (Table 5-2). This trend was also observed during the various ethanol fractions examined in this study. As expected, the treated iron

degraded PCE in solution more rapidly than the untreated iron (Table 5-3). This was attributed to the improved number of sorption sites on the treated iron due to acid treatment. Faster dechlorination rates due to acid washing seen in this research were similarly reported by Matheson and Tratnyek (1994) and Burris et al. (1995) in their experimental tests.

The NiFe was found to degrade PCE faster than the other forms of iron (Table 5-2 and 5-3). Similar to other reductive metals in bimetallic complexes, the effectiveness of the nickel-plated iron was most likely due to the ability of nickel to facilitate electron transfer, so reduction could proceed more rapidly (Korte et al., 1997). It has also been stated that the nickel-plating reduces the formation of oxides on the iron surface, thereby, increasing the relative number of sorption sites when compared to the non-bimetallic iron over the duration of the experiment (Wang and Zhang, 1997). The faster degradation rate of PCE with NiFe was also consistent over the range of ethanol fractions investigated (Tables 5-2 and 5-3).

#### Cosolvent Effects

Ethanol was added at four different volume fractions (0%, 10%, 30%, and 50%) to determine how cosolvents would affect the PCE degradation in the presence of iron. Increasing the ethanol fraction in the PCE solutions was found to decrease the degradation rates regardless of iron type or concentration level (Table 5-2). This effect of ethanol was attributed to its influence on sorption of the PCE to the iron surfaces. Sorption isotherms were made for each of the modified iron types (Figures 5-6 thru 5-8).

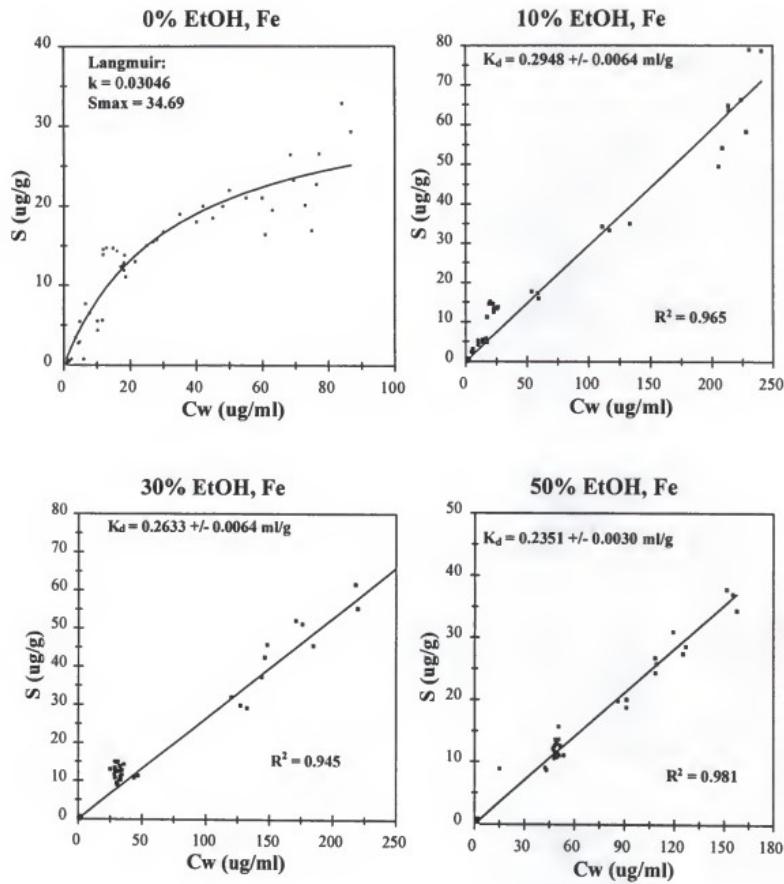


Figure 5-6 Sorption isotherms of PCE partitioning onto untreated zero-valent iron as a function of different ethanol fractions in solution

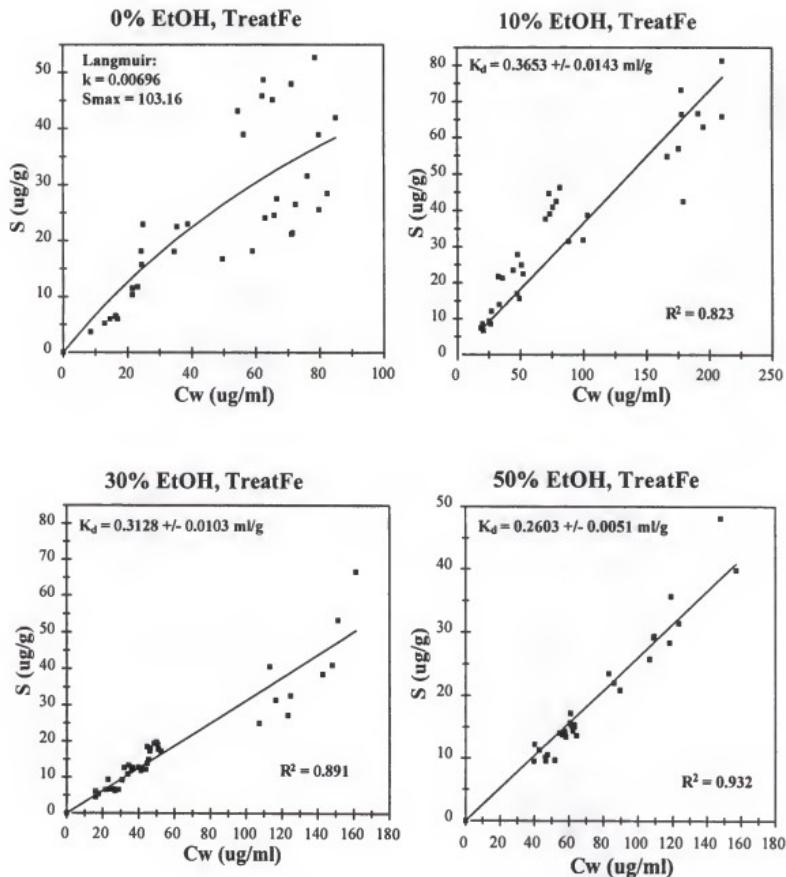


Figure 5-7 Sorption isotherms of PCE partitioning onto acid treated iron as a function of different ethanol fractions in solution

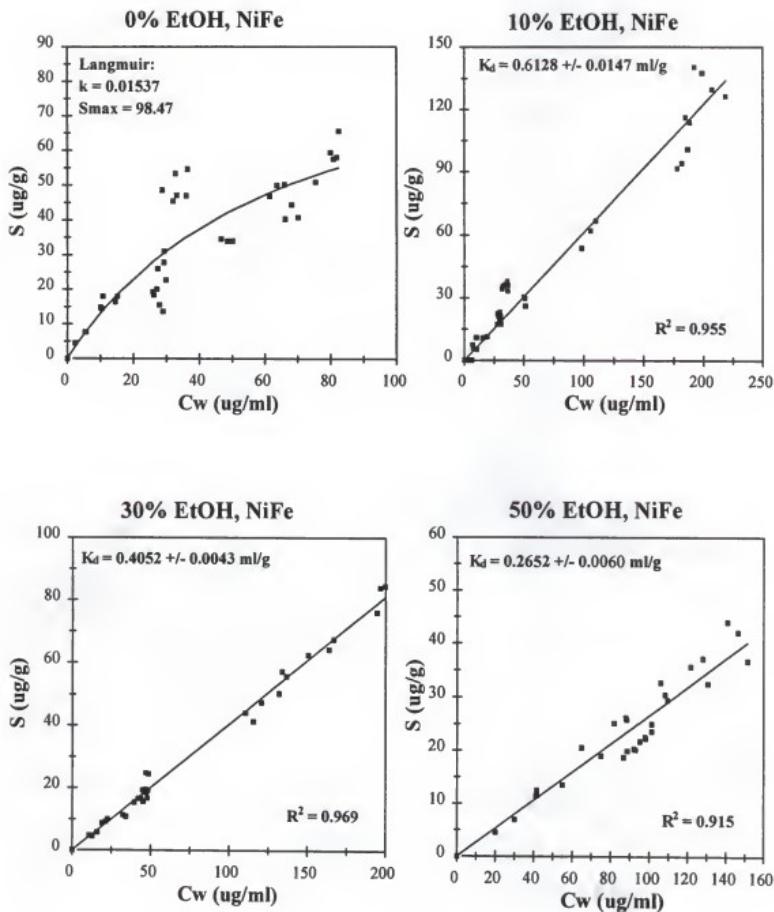


Figure 5-8 Sorption isotherms of PCE partitioning onto nickel-plated iron as a function of different ethanol fractions in solution

For each of the 0% ethanol solutions, PCE was found to adsorb to the iron surfaces in a manner best described by the Langmuir sorption isotherm relationship. These results agreed with the assertion made by Burris et al. (1995). This relationship was described by Domenico and Schwartz (1990) with the expression:

$$S = \frac{S_{\max} k C}{1 + k C}$$

where S is  $\mu\text{g}$  of PCE sorbed / g of Fe sorbent and  $S_{\max}$  is the maximum estimated value of the sorbed PCE mass to the iron surface; C is  $\mu\text{g}$  of PCE in solution / ml of bulk solution; and k is generalized Langmuir coefficient. The Langmuir sorption coefficients are seen in the 0% ethanol data plots provided in Figures 5-6 through 5-8.

For the aqueous solutions in which contained 10% ethanol and greater, linear sorption isotherm relationships were found. The following equation was used in the development of these isotherms:

$$S = K_d C$$

where; and  $K_d$  is ml of PCE / g of Fe sorbent and is known as the partition (or sorption) coefficient. Larger  $K_d$  values (Table 5-5) indicate a greater tendency of PCE to adsorb to the surface of the solid particles. This meant that as more PCE partitioned to the iron surfaces, the degradation rate would increase, which was what the results of this study showed (Figure 5-9). In Figure 5-9, the rate constant describing PCE loss was seen to increase as the sorption coefficient increased for every iron surface type investigated in this study, again showing that PCE adsorption to the iron surface plays an influential role in its degradation.

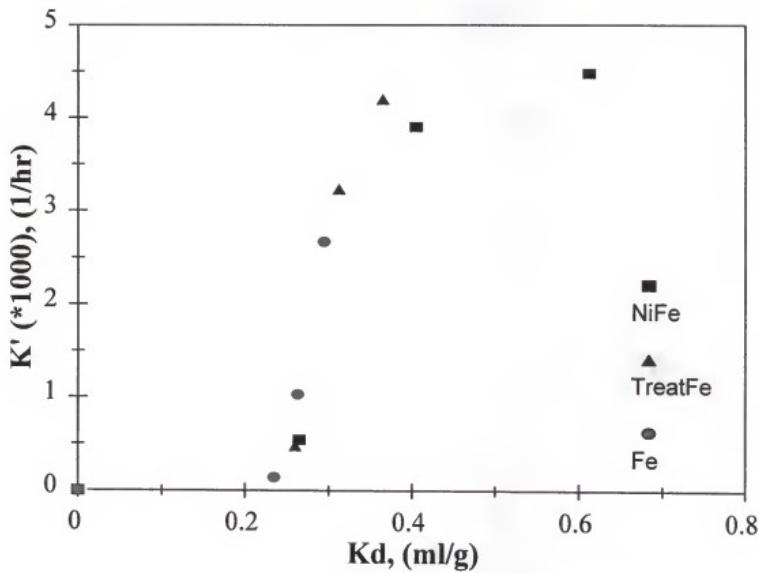


Figure 5-9 Degradation rates of PCE as a function of the sorption coefficients for multiple iron surfaces studied

The natural log of relative PCE concentrations (C/Co) over time, degradation rate constants, and partition coefficients were also plotted based on ethanol fractions (Figures 5-10 through 5-12). These figures better displayed how the increase in ethanol fraction resulted in decreased overall PCE degradation, decreased rates of degradation, and decreased partitioning of PCE to the various modified iron surfaces.

Finally, although high cosolvent fractions can be used to increase the removal of PCE and other NAPLs from the subsurface, their increased percentages would reduce the effectiveness of dechlorination by iron. Although it has been shown that modification of the iron surface would improve PCE dechlorination, this improvement is also greatly diminished by the presence of cosolvents in solution.

In applying this information to possible field use, Tratnyek et al. (1997) stated that PCE/iron contact time is one of the most critical issues in using dechlorination as a treatment technique. The ex-situ design must provide a sufficient contact time of iron with contaminated solution to ensure sufficient degradation of the pollutants. Understanding that adsorption of the contaminant to the iron surface is the major factor in its degradation, solutions with increasing cosolvent fractions would require larger treatment containers or slower flow rates through them. These modifications would provide the longer contact times necessary for possible adsorption of contaminants in solutions where cosolvent is present.

#### Degradation By-Products

The focus of this research was not to study PCE by-products; however, TCE and DCE, which are thought to be major by-products of PCE degradation (Arnold and

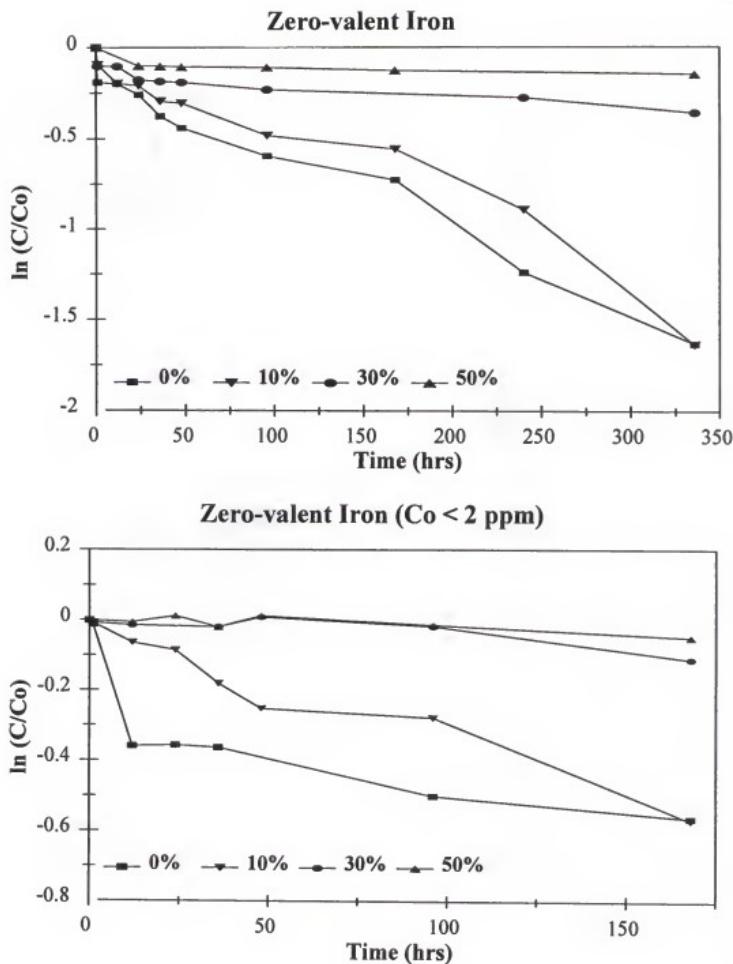


Figure 5-10 Degradation of PCE in aqueous solutions in the presence of modified iron surfaces

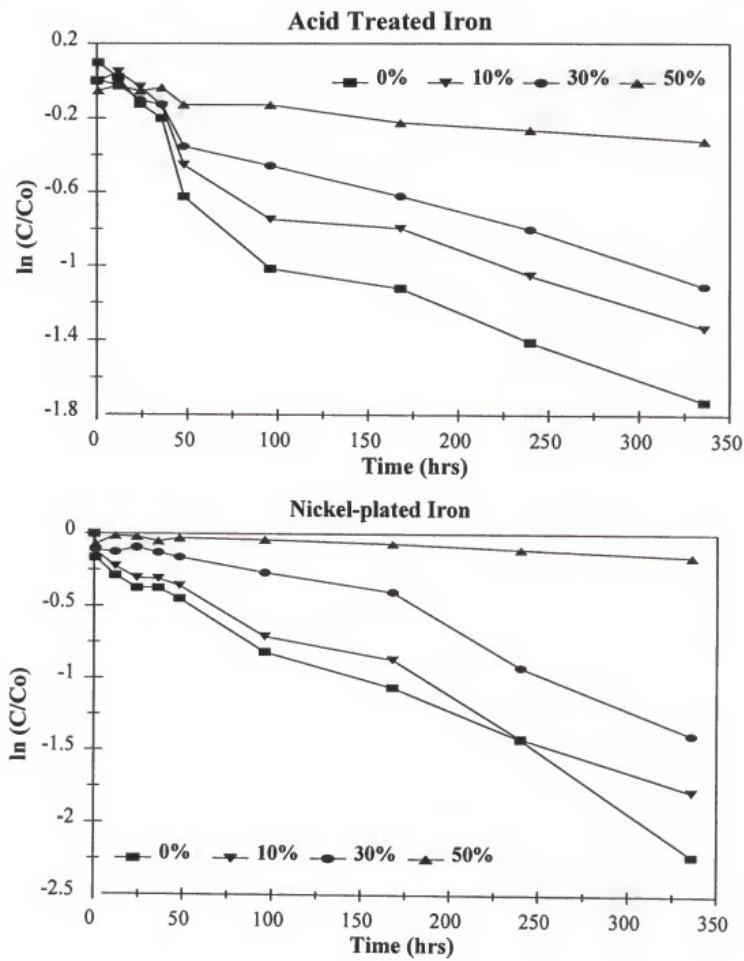


Figure 5-10 contd.

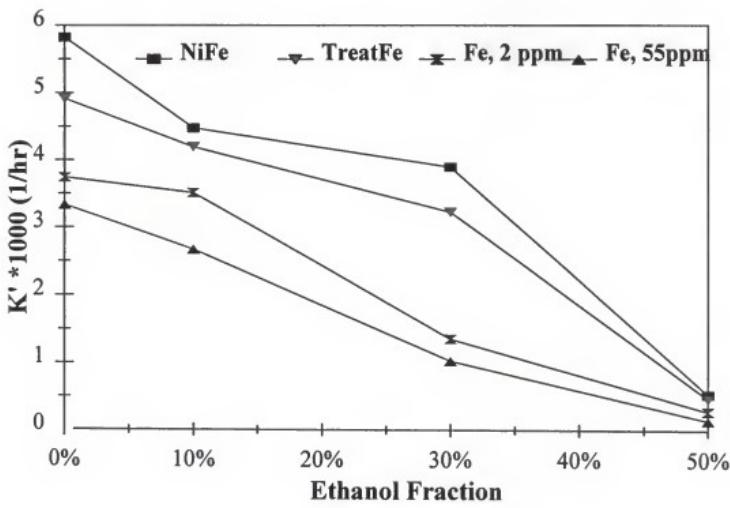


Figure 5-11 Degradation rates of PCE in the presence of modified iron as functions of ethanol fraction

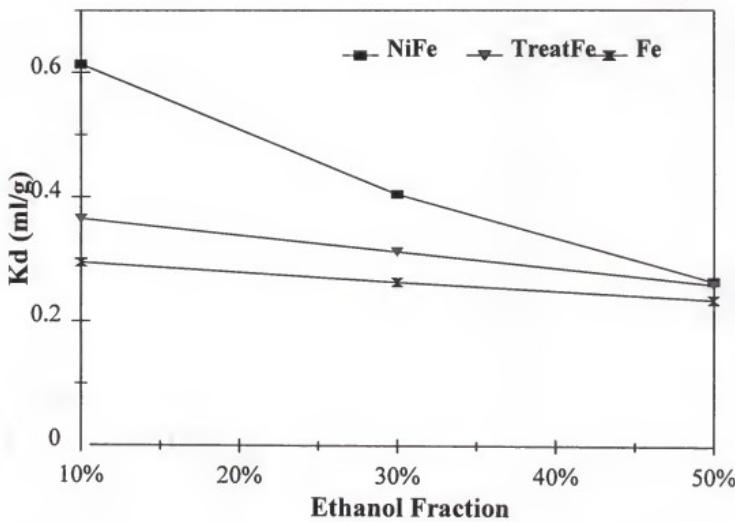


Figure 5-12 Sorption coefficients of PCE onto modified iron surfaces as functions of ethanol fraction

Roberts, 1998), were monitored. DCE was found never to be produced in enough quantities to be detected by the analysis used in this research. Production of TCE, on the other hand, was detected in small amounts. As seen in Figures 5-13 through 5-16, TCE was produced as PCE degraded, suggesting a logical correlation between the PCE dechlorination and TCE presence in the systems. Also supporting this observation, the amount of TCE produced was generally negligible with increasing ethanol fractions and decreasing PCE degradation rates. It was also noted that as time continued, the TCE itself was also seen to decrease or degrade. If smaller chlorinated by-products of TCE degradation were produced, they were at much smaller quantities than could be detected with analytical equipment employed in this research. Also, as less PCE was degraded, usually seen at higher ethanol fraction solutions, not much, if any, TCE was detected (Figure 5-13d). This raises concerns that TCE formed during degradation competes for sorption reaction sites with PCE, which may affect degradation. Burris et al. (1995) reported that this competition was a distinct possibility for a finite number of sorption sites. In this research, the sorption site saturation point was not reached because the sorption isotherms displayed larger sorption masses of PCE were attainable; further, TCE was seen to be produced and then decreased while PCE simultaneously decreased steadily at a constant pseudo first-order degradation rate. However, as previously stated, a more exhaustive by-product study of dechlorination reactions would need to be conducted before questions such as those could be answered conclusively.

Consistent with the observation of previous research (Gillham and O'Hannesin, 1994; Mustikian et al., 1995), a headspace was observed to form in the reactor vials over

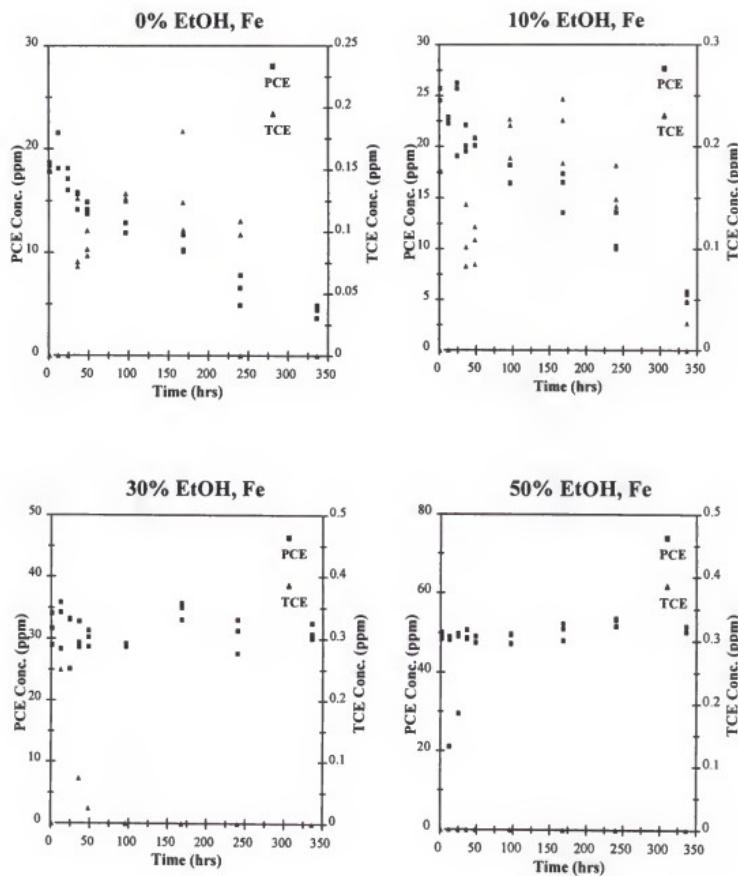


Figure 5-13 Concentrations of PCE and TCE in aqueous solution as functions of time in the presence of zero-valent iron and different cosolvent fractions

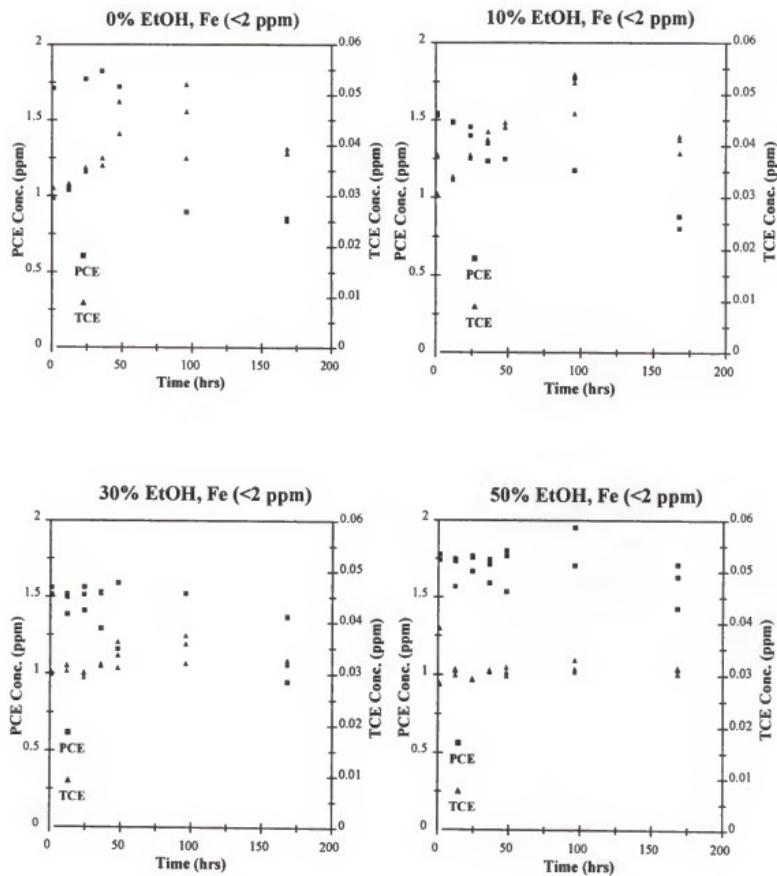


Figure 5-14 Concentrations of PCE and TCE in aqueous solution ( $C_o < 2$  ppm) as functions of time in the presence of zero-valent iron and different cosolvent fractions

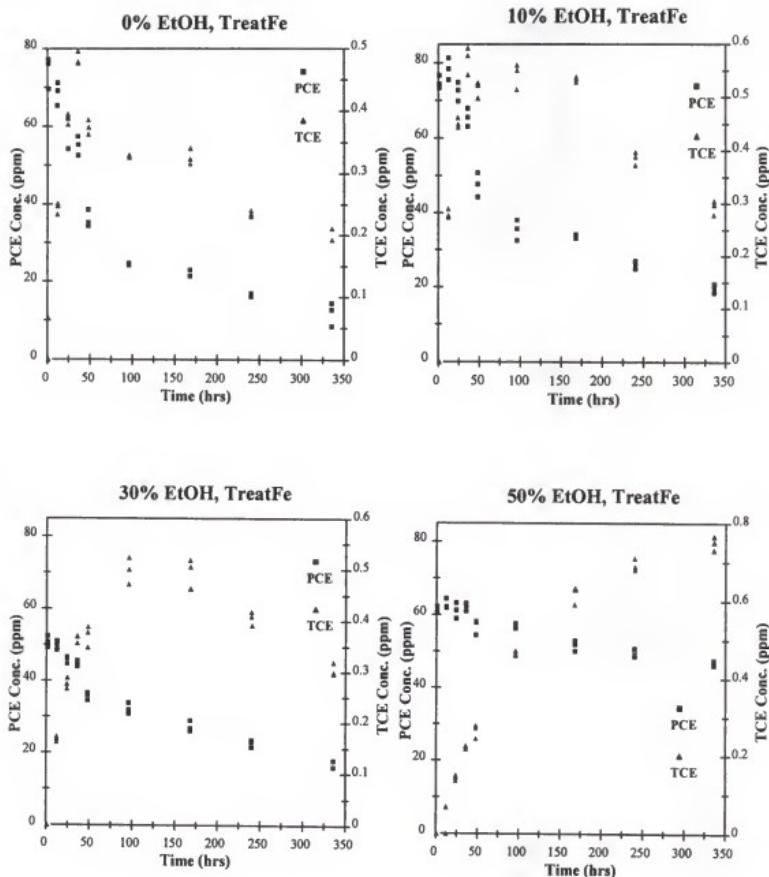


Figure 5-15 Concentrations of PCE and TCE in aqueous solution as functions of time in the presence of acid treated iron and different cosolvent fractions

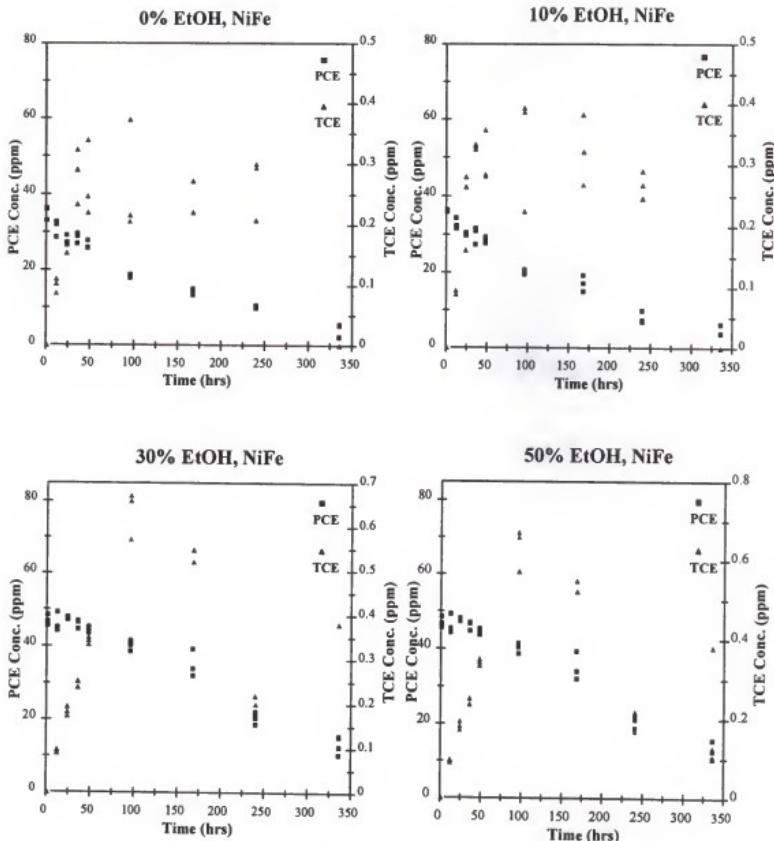


Figure 5-16 Concentrations of PCE and TCE in aqueous solution as functions of time in the presence of nickel-plated iron and different cosolvent fractions

time. Although not quantified, based on the above references, the major components of the headspace were expected to be hydrogen and nitrogen. Hydrogen was produced relative to the dissociation of water in the redox reactions seen in the vials. Nitrogen was stated by the earlier references to be produced from air possibly dissolved in stock solutions. It was also noted in the results of this study that as ethanol fraction increased, less headspace was developed. This supports the observation that as degradation improved with lower cosolvent fractions, gas formation from the reaction also increased.

Slight formation of iron oxides (rust) was also noted to appear on the iron surface over the duration of the experiment. Generally, the longer the rotation time, the more dark brown oxides were observed on the iron surface. It was also noted that with increasing ethanol fractions, lesser amounts of these oxides were observed. This would suggest that as adsorption decreased with greater cosolvent fractions, so would the surface reactions that would produce iron oxides, as well as the previously mentioned headspace gas.

Further research is being conducted into methods of regeneration of the metal after use. Suggestions to this point have centered on the use of acids for oxide removal and surface cleaning (Korte et al., 1997). Such possibilities increase the appeal of using this method of treatment for degrading chlorinated effluents from contaminated sites.

#### Cost Analysis

Tim McHale of ManTech Environmental Services Corporation quoted that the treatment of the PCE waste by DuPont in Deepwater, New Jersey was going to cost \$1.25/gallon. An estimated waste volume of 20,000 gallons would cost \$25,000 to treat

after removal from the site. Employing the same volume of solution to mass of iron ratio (4:1) from the lab experiments to the scale-up design would dictate that almost 21 tons of iron would be required to treat the effluent volume. Master Builders, Inc. in Cleveland, Ohio quoted a cost of approximately \$11,500 to purchase this amount of iron. Assuming negligible power inputs and utilizing the experimental volume to mass ratio, the cost for employing iron treatment method is cheaper than treating the PCE solution by DuPont. Application in a flow through design could further reduce costs. Based on this cursory cost analysis, it seems the use of iron as an ex-situ treatment method is an economically feasible option for destruction of PCE in cosolvent flushing waste effluents.

### Conclusions

The purpose of this research was to evaluate the effectiveness of ex-situ zero-valent iron in treating a solution which contained perchloroethylene. Modifications to the iron and different fractions of cosolvent (ethanol) added to the solution were included in the investigation to observe how these variations would affect the PCE degradation.

The experimental batch tests results showed that PCE was found to degrade in the presence of zero-valent iron. These degradation reactions were found to be pseudo first-order with respect to PCE loss over time, which agreed with results reported from previous research.

Comparing different concentrations of PCE, it was found that the degradation of a higher (~55 ppm) concentration of PCE with untreated iron was seen to occur slower than that of a much lower PCE concentration (<2 ppm). This seemed to indicate that a fewer

number of PCE molecules may find more available sorption sites on the iron surface, therefore, these smaller number of molecules can be adsorbed and degraded faster than that of a larger number of molecules.

In this research, different iron surfaces were studied to determine their effect on PCE degradation. In degrading PCE, the results showed that the nickel-plated iron (NiFe) was the most effective, followed by the acid pretreated zero-valent iron (TreatFe), and, finally, the untreated zero-valent iron.

For solutions with no ethanol cosolvent present, Langmuir sorption isotherms described PCE adsorption to the modified iron surfaces. However, linear sorption isotherms were exhibited for solutions in which ethanol was present. A relationship between degradation rate and adsorption showed that as adsorption to the iron surface increased, so did the degradation rates. Experimental results showed that increased ethanol fractions resulted in decreased adsorption of PCE to the iron surface which, consequently, led to the decreased rates of PCE degradation.

By-product formation was not a focus in this study, but TCE was observed to be produced as PCE degraded, which implied an apparent correlation between the PCE dechlorination and TCE presence in the systems. Increasing ethanol fractions and decreasing PCE degradation rates reduced TCE produced to negligible amounts. However, total degradation products of PCE dechlorination have yet to be quantified.

Overall, it was concluded that although cosolvent fractions increase the removal of PCE and other NAPLs from the subsurface, their presence would reduce the effectiveness of dechlorination by iron, even if the iron surface was modified.

## CHAPTER 6

### EVALUATION OF SONOCHEMICAL DESTRUCTION OF CHLORINATED WASTE SOLUTIONS

#### Introduction

An area of concern for environmentalists has been the protection and conservation of groundwater drinking supplies. Discharge of various chlorinated solvents by either industrial processes, military operations, or private businesses have led to extensive soil and groundwater contamination. Chlorinated organics are of special concern not only due to their environmental impacts, such as causing ozone depletion (Hooker and Klabunde, 1994), but also because of their impacts on human health. Several produce adverse effects on the human central nervous system, while others are suspected carcinogens and are listed as Environmental Protection Agency priority pollutants (Hua and Hoffmann, 1996). It is important to reduce the use of such compounds, find methods of removing them from the environment, and means for safely destroying them.

Contamination of groundwater resources has promoted the development of various technologies to remediate polluted subsurface environments. However, remediation of groundwater contaminated with dense chlorinated solvents is difficult using conventional pump-and-treat methods due to inefficiency in extracting organic contaminants from heterogeneous subsurface environments (Fennelly and Roberts, 1998).

Recently, the use of additive chemicals, such as cosolvents and surfactants, in specially designed pump-and-treat flow patterns have experienced success in removal of these contaminants from the subsurface environment (Wood et al., 1990; Augustijn et al., 1994; Parker et al., 1994; Imhoff et al., 1995; Rao et al., 1997). Once removed from the soil, the problem remains regarding how to manage the waste fluids during in-situ flushing.

Slow degradation processes, such as passive dechlorination with zero-valent iron (Gillham and O'Hannesin, 1994; Tratnyek et al., 1997) and treated iron (Burris et al., 1995; Liang et al., 1997) have produced successful results in treating chlorinated solutions. These systems generally produced gradual transformations of the chlorinated compounds to a less chlorinated, and usually, a less harmful state. Another method of treating of chlorinated compounds that focuses on aggressive destruction contaminant is known as sonication. This ex-situ process has gained some recognition in its effectiveness in destruction of chlorinated contaminants (Bhatnagar and Cheung, 1994; Hua et al., 1995a; Hung and Hoffman, 1998). The sonicated solutions experience cavitation in which high temperature and pressure spots in the solution result in extremely strong oxidation and reduction reactions which destroy the chlorinated contaminants.

The purpose of this research was to study and evaluate the ability of sonication to treat perchloroethylene (PCE) in cosolvent mixtures. Different PCE concentrations with various cosolvent percentages were subjected to sonication treatment and monitored over time. This provided information on the effectiveness of sonication for destroying PCE at different concentrations and how different cosolvent fractions, used in removing the DNAPL from the subsurface, might affect this treatment method.

BackgroundSonochemistry

Sonochemistry is the basis for the degradation investigated in this research. There are four types of sonochemical reactions (Henglein, 1987): 1) the acceleration of conventional reactions to increase intermolecular collisions, such as hydrolysis; 2) redox processes in aqueous solution; 3) the degradation of polymers; and 4) the decomposition of and reactions in organic solvents. Reactions of type 1 are of interest in preparative chemistry. Ultrasound has an accelerating effect in many organic syntheses, sometimes less by-products are formed and the yield of the main product is increased, and reactions may be carried out at a lower temperature or lower excess pressure. Type 2 reactions may play a role in the irradiation of biologically important molecules in aqueous media. These reactions often resemble those initiated by ionizing radiations. The third type of sonochemical reaction is the degradation of macromolecules in solution. The fourth sonochemical reaction, most relevant to the current research, involves the decomposition of organic liquids with the production of free radicals as intermediates in solution (Henglein, 1987; Petrier et al. 1992).

Sonication, also known as ultrasonic irradiation and sonolysis, is the use of ultrasound to initiate high-energy chemistry. The chemical effects of ultrasound do not come from a direct interaction with molecular species. Instead, sonochemistry derives principally from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid (Suslick, 1990; Hua et al., 1995b). Cavitation is the fundamental nonlinear acoustic process that serves as a means of concentration of the diffuse energy of

sound in liquids (Suslick, 1990). This formation of cavities in liquids is a nucleated process, in which bubbles form at weak points in the liquid, such as gas-filled crevices in suspended particulate matter or from transient microbubbles from prior cavitation events due to applied ultrasonic energy. As a cavity bubble containing water vapor, dissolved gases, and high vapor pressure solutes grows, it absorbs the energy from the surrounding liquid field. Margulies et al. (1985) provided the following equation for dynamics of cavitation field evolution:

$$\frac{d\eta}{dt} = \frac{\eta}{iT_o} - K_c \eta^2 + \frac{j\eta}{iT_o}$$

where  $\eta$  is the local concentration ( $M/L^3$ ) of cavitation at time,  $T$ ;  $K_c$  is the rate constant of cavitation bubbles coalescence ( $1/T$ );  $j$  is the average number of fragmentation bubbles after one bubble has split (dimension less);  $T_o$  is the period of acoustic oscillations ( $T$ );  $i$  represents the average number (dimension less) of bubble pulsations (before "collapse"). Integrating from  $0 \rightarrow t$  and  $\eta_o \rightarrow \eta$  provided the following function to describe cavitation concentration as a direct function of time:

$$\eta(t) = \frac{\eta_\infty \eta_o}{\eta_o + (\eta_\infty - \eta_o) \exp(-\eta_\infty K_c t)}$$

where  $\eta_\infty$  represents the stationary bubble concentration ( $M/L^3$ ) =  $(j-1)/i K_c T_o$ .

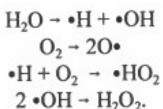
However, once this cavity becomes overgrown, it can no longer efficiently absorb energy and can no longer sustain itself. Implosion follows as the surrounding liquid rushes in, which results in the compression of gas that generates heat and high pressure gradients. This causes a short-lived, localized hot-spot in an otherwise cold liquid. This

hot-spot is the source of homogeneous sonochemistry (Henglein, 1987; Suslick, 1990; Cheung et al., 1991; Moholkar and Pandit, 1997). Suslick (1990) and Hua et al. (1995b) agreed that due to the transient nature of the cavitation event, direct measurements of the conditions such as temperature and pressure generated during bubble collapse are unavailable. However, Suslick (1990) stated that estimates were conducted by using competing unimolecular reactions whose rate dependence on temperature were already known from previous measurements. Temperatures and pressures of an imploding cavity have been determined to be 5500°C and 500 atm (Suslick, 1990; Cheung et al., 1991; Bhatnagar and Cheung, 1994). In these critical spots, substrates such chlorinated hydrocarbons, pesticides, phenols, and esters are transformed into short-chain organic acids, CO<sub>2</sub>, and inorganic ions as the final products (Hua et al., 1995a).

The reactions that take place at the gas-liquid interface of the bubble are similar to those witnessed in high-temperature combustion (Kotronarou et al., 1992; Petrier et al., 1992), but strong reduction and oxidation reactions have been observed due to the formation of the free radicals (Hua and Hoffmann, 1997). Radicals of water, once generated, travel to the bulk liquid phase where they initiate secondary oxidation reactions. The products of water sonication (H, OH, HO<sub>2</sub>, etc.) are highly reactive and are capable of oxidizing the target compound. The solute molecule breaks down as a result of free radical attack generated as a result of high intensity ultrasonic waves. In the case of chlorinated organics, the high temperature and pressure in the cavitation bubbles provide the activation energy required to cleave the C-Cl bond. Cheung et al. (1991) and Bhatnagar and Cheung (1994) both reported successful results in destruction of

chlorinated compounds by sonolysis.

Hua and Hoffman (1997) offered the following equations to depict the sonochemical reactions for production of highly oxidizing free radicals:



Kotronarou et al. (1992) stated that sonochemical reactions are not always dominated by free radical reactions. Sonochemical reactions are normally characterized by the simultaneous occurrence of pyrolysis and radical reactions, especially at high concentrations. Volatile solutes will undergo direct pyrolysis or combustive reactions within the gas phase of the collapsing bubbles or within the hot interfacial region. It was reported that pyrolysis in the interfacial region is predominant at high solute concentrations, while at low solute concentrations, free-radical reactions are likely to dominate (Kotronarou et al., 1992).

Oxidative species from different sources are used to degrade toxic organic pollutants present in water (Petrier et al., 1992). Ultrasonication, which is able to provide such reactive intermediates, has shown some efficiency in the degradation of organic pollutants present in water (Cheung et al., 1991; Kotronarou et al., 1992; Petrier et al., 1992). But, a product of degraded carbon compounds, CO<sub>2</sub>, was shown by Petrier et al. (1992) to inhibit some sonochemical reactions, especially in degradation situations.

Hua et al. (1995a) discussed sonochemical degradation in a parallel-plate near-field acoustical processor. In that study, it was concluded that faster degradation rates at

higher power densities (power input/volume of solution) result for a higher number of reactive sites, known as cavitation events or bubbles, in solution. Hua et al. (1995) further explained that an increase the number of bubbles in solution is dependent upon the power or energy applied to the system volume, and can be estimated by the following equation:

$$E = \frac{4}{3} PNR^3_{\max}$$

where E is the energy required to expand a population of bubbles in solution; P is the magnitude of the hydrostatic and acoustic pressure; N is the number of bubbles in solution;  $R_{\max}$  is the maximum radius of the bubble before it collapses. This led to the conclusion that as the number of bubbles increases the power density increases, even though the number of chemical events per bubble is not known (Hua et al., 1995a).

Hua and Hoffmann (1997) later stated that ultrasonic irradiation at higher frequencies leads to greater enhancements in reaction rates compared to lower frequencies, and that these frequencies affect the reaction environment by determining resonant bubble radius through the following relationship:

$$\rho\omega_r^2 R_r^2 = 3KP_0$$

where  $\rho$  is the density of water;  $\omega_r$  is the resonance frequency;  $R_r$  is the resonant radius;  $P_0$  is the pressure in the liquid, and K is the ratio of the specific heats ( $C_p/C_v$ ) and is known as the polytropic index.

Hua et al. (1995b) further predicted that a cosolvent, in their case methanol, may slow down or inhibit sonolysis of most organic molecules. This prediction was based on

the cosolvent's preferential accumulation at the bubble interface during sonication. Data reported by Hua et al.(1995b) showed that rate constants of solutions without methanol,  $-0.016 \text{ min}^{-1}$ , were around 63% larger than those solutions which included 25% methanol,  $-0.010 \text{ min}^{-1}$ , sonicated under similar conditions. However, no further elaboration on these results were made, perhaps because this was just an aside discovery to their research focus.

#### Advantages Over Other Modern Treatment Methods

Hua et al. (1995a) showed that ultrasonic radiation compared favorably with other modern treatment methods, including bacterial reduction or oxidation, carbon adsorption, membrane solvent extraction, ozonolysis, and the Fenton reaction. Most of the previously mentioned techniques resulted in >90% degradation or removal of p-nitrophenol contaminant within hours. However, Hua et al. (1995a) stated that ultrasonication offers the advantage of complete destruction over carbon adsorption and membrane extraction. In comparison to certain biological systems, degradation by ultrasonic irradiation occurs over concentration ranges varying by orders of magnitude and is not limited by relatively low substrate concentrations. Hua et al. (1995a) also added that cavitation chemistry does not exhibit complex pH effects that are observed during ozonolysis of the substrate.

Other researchers also reported successful results in degradation of potential contaminants by sonication. Bhatnagar and Cheung (1994) reported destruction percentages between 72 to 99.9% for sonication of methylene chloride, chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, TCE, and PCE from

initial concentrations ranging from 50 to 350 mg/L. While Cheung et al. (1991) reported success in the sonochemical destruction of methylene chloride, carbon tetrachloride, 1,1,1-trichloroethane, and trichloroethylene in the 100 - 1000 mg/L range.

#### Materials and Methods

The experimental setup consisted of a Heat Systems W-375 ultrasonicator with a stainless steel probe. The W-375 ultrasonicator is capable of delivering 350 W of ultrasonic energy at maximum output setting and 100% of its rated power. In this study, the sonicator was operated at its maximum output setting with a duty cycle of 60%, which delivered over 40% of the maximum energy (approximately 150 W) to the reactor vessel.

Several concentrations of PCE solutions were mixed for treatment by sonication. These solutions included concentrations of 25, 50, 75, 100, and 150 ppm of PCE in aqueous solutions. Differing percentages of ethanol were also incorporated to represent different cosolvent amounts that might be used in remediation of chlorinated compounds from subsurface systems. These percentages included 0%, 10%, 30% and 50% of ethanol in solutions of the various aforementioned PCE concentrations.

Each experimental solution was mixed to a volume of 500 mL, and transferred into an Erlenmeyer flask with an output nozzle which was then placed in the sonicator's protective cabinet (Figure 6-1). The steel probe of the sonicator was then placed nearly half way down into the PCE solution before the apparatus was turned on. A teflon line that ran from the bottom of the Erlenmeyer flask and out of the output nozzle located at

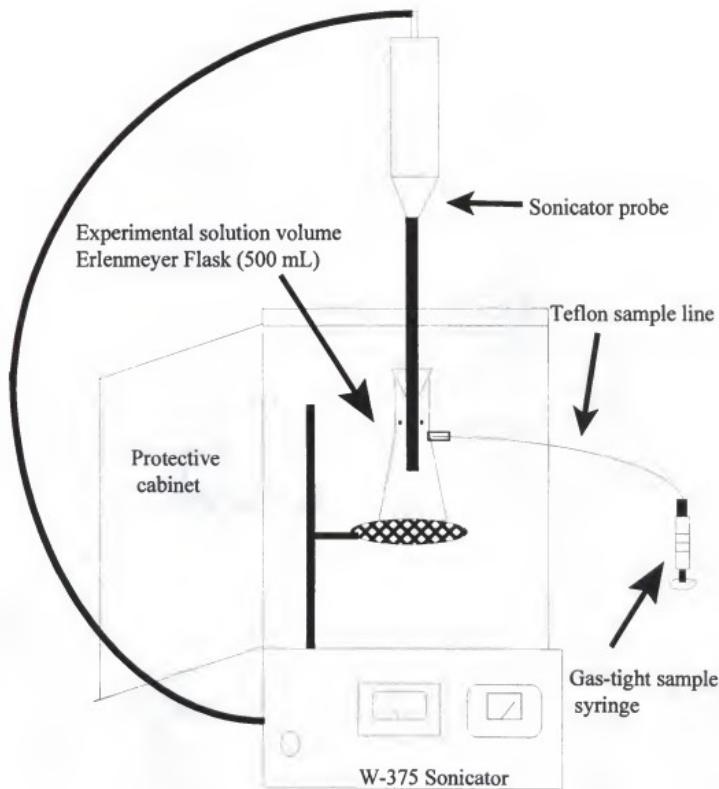


Figure 6-1 Schematic of sonication experimental setup

the top of the flask was used to withdraw liquid samples over the duration of the experiment. This line was surrounded by parafilm and taped closed around the nozzle opening to make the closure gas-tight. A glass and teflon gas-tight syringe was used to withdraw the liquid samples from the teflon line. Finally, the samples were transferred into 2 mL vials for analysis. A rubber stopper with a hole just big enough for the steel probe of the sonicator was used to seal the top of the system.

The Erlenmeyer flask in the sonicator was placed in a plastic beaker into which ice was added. This outer flask was used to maintain the temperature of the system to under 33°C at outer surface of the liquid to minimize possible volatilization losses due to excessive heat. Due to the high temperatures generated by the sonication system, the melted ice was continually replaced throughout the experiment. The temperature of the liquid that surrounded the Erlenmeyer flask was checked constantly by thermometer. Figure 6-2 displays the results obtained during a test which indicated there was minimal PCE loss due to volatilization or leakage. PCE was additionally sampled with just stirring taking place in the flask to determine if the violent sonication would aid in volatilization as well. Figure 6-3 shows that PCE loss during stirring was more than insignificant ( $k = -0.179 \text{ hr}^{-1}$ ), which showed the collision forces that occur during sonication of PCE are not trivial in degradation. The intermolecular collisions that occur during mixing may be important in the cavitation process that happens inside the liquid volume; however, its influence may not necessarily be dominant. This assertion will be discussed later.

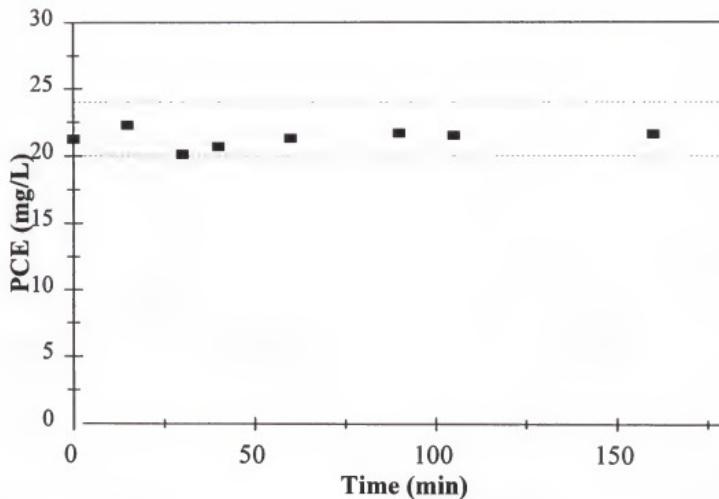


Figure 6-2 PCE concentration in experimental sonication configuration without applying sonication

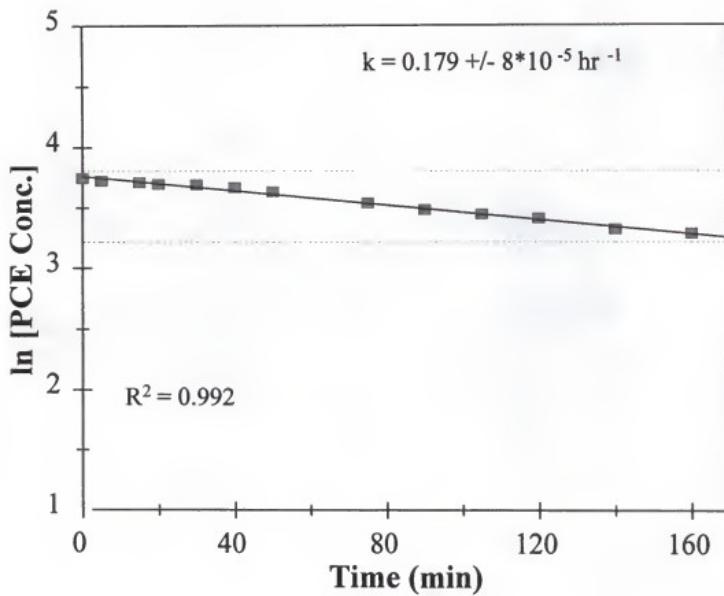


Figure 6-3 PCE concentration over time due to stirring

Analysis was conducted on a Shimadzu-10A High Performance Liquid Chromatograph (HPLC) System fitted with a Supelco PAH-C18 Column. The system was equipped with a UV-VIS Detector set a wavelength of 230 nm. The mobile phase was run at a velocity of 2 mL/min, and contained 65% methanol and 35% HPLC water.

### Results and Discussion

Sonication was used to treat PCE aqueous solutions to evaluate its potential effectiveness in treating effluent from a subsurface remediation system. Various PCE concentrations were studied to determine if the amount of PCE would affect the degradation by sonication. Further, multiple percentages of ethanol were employed to represent varying cosolvent percentages that might be present in a effluent from remediation of PCE contaminated site, and how this factor might affect degradation of PCE by sonication.

Individual samples taken from the sonication experiment resulted in pseudo first-order kinetic degradation of the PCE aqueous solutions (Figures 6-4 through 6-8). This was determined from the slope of the  $\ln[\text{PCE concentration}]$  versus time plot. This pseudo first-order kinetic relationship was expected in sonication of chlorinated solutions and had previously been reported by Hua et al. (1995b), Hua et al. (1996), Petrier et al. (1998), and Rajan et al. (1998). The degradation results gathered in this research coincided with results reported in the literature (Figure 6-9) despite the minor variations in sonication procedures. PCE degradation data from sonication experiments conducted by Bhatnagar and Cheung (1994) were similar to the data reported in this research for

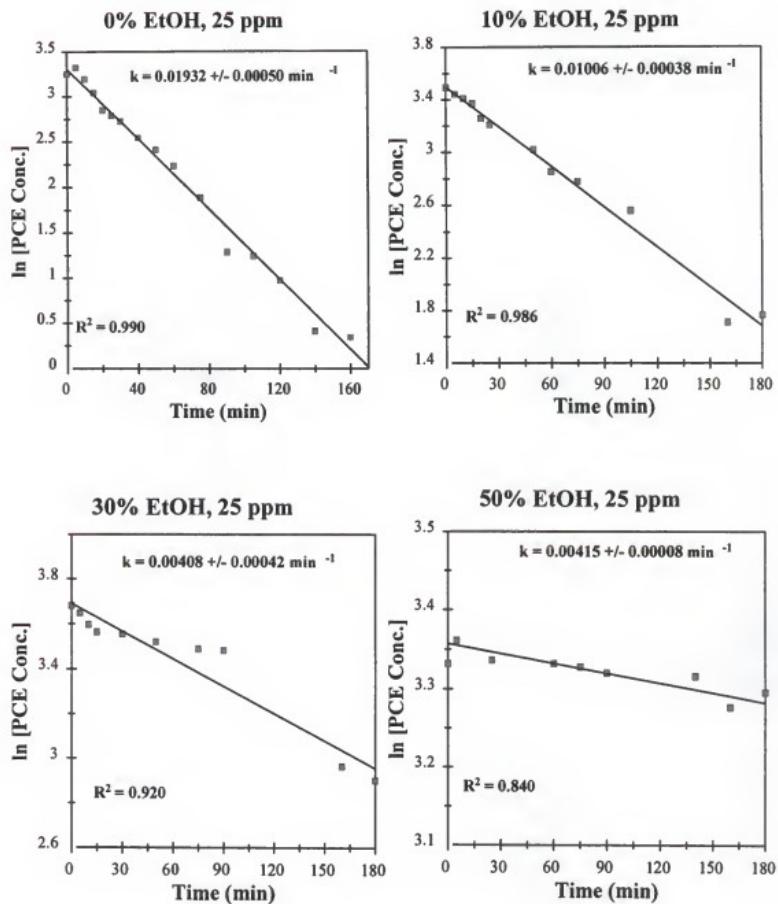


Figure 6-4 Pseudo first-order degradation of PCE in aqueous solutions by sonication for different ethanol fractions ( $C_0 \approx 25 \text{ ppm}$ )

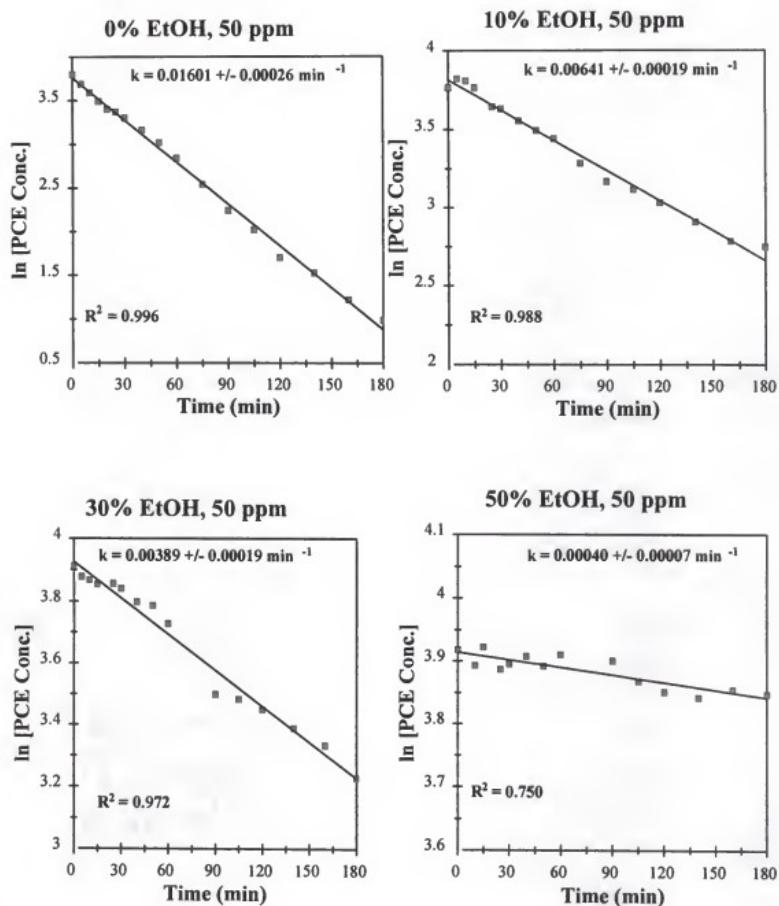


Figure 6-5 Pseudo first-order degradation of PCE in aqueous solutions by sonication for different ethanol fractions ( $C_0 \approx 50 \text{ ppm}$ )

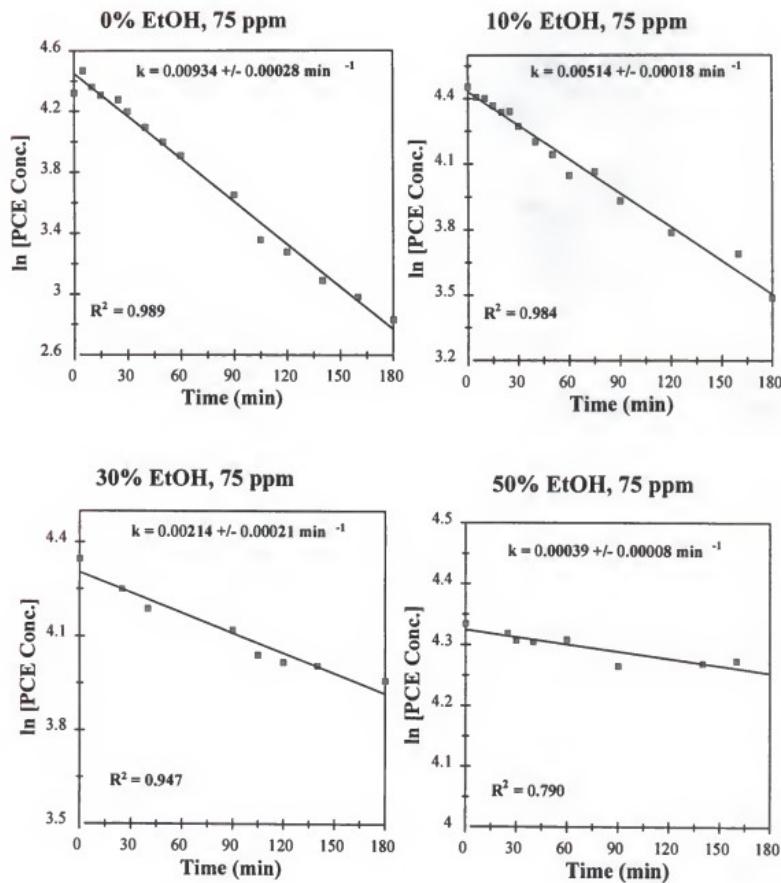


Figure 6-6 Pseudo first-order degradation of PCE in aqueous solutions by sonication for different ethanol fractions ( $\text{Co} \approx 75 \text{ ppm}$ )

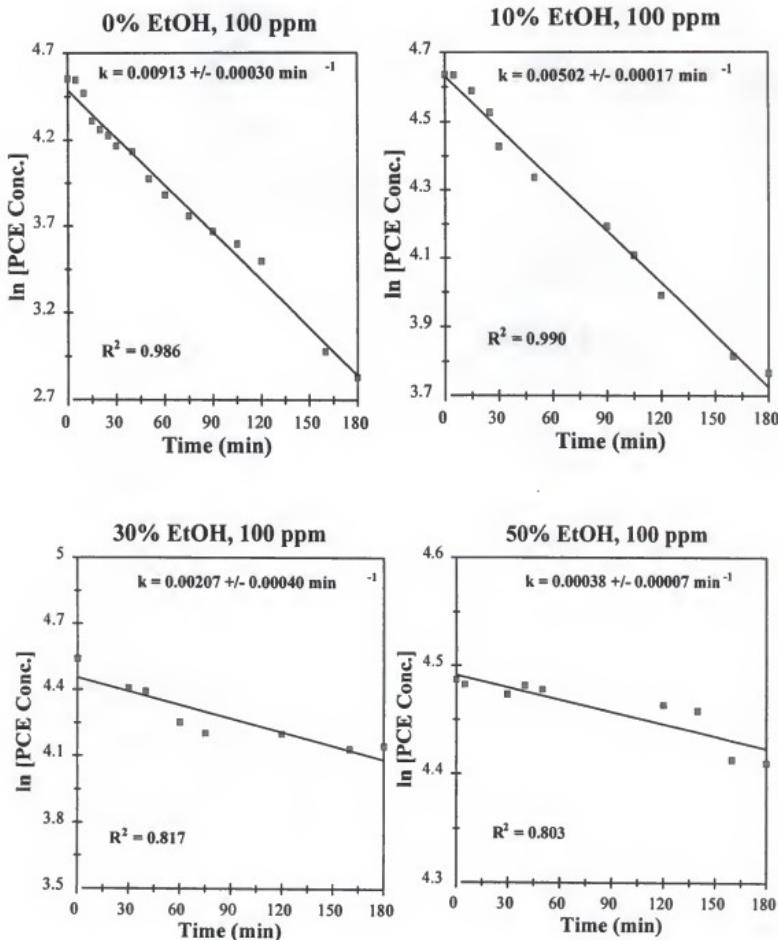


Figure 6-7 Pseudo first-order degradation of PCE in aqueous solutions by sonication for different ethanol fractions ( $C_0 \approx 100 \text{ ppm}$ )

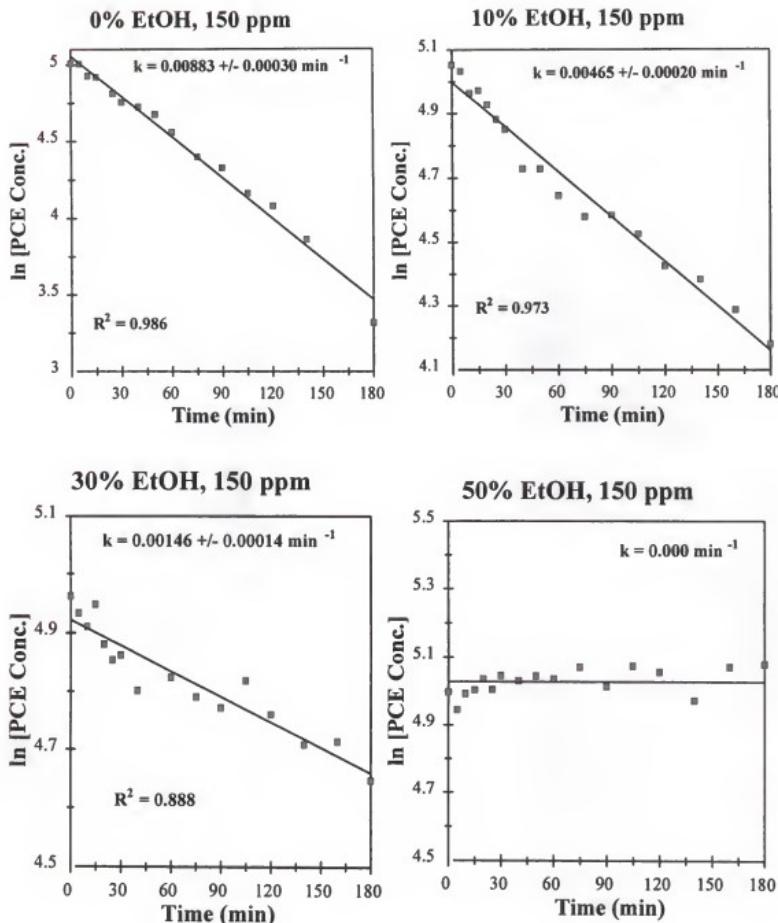


Figure 6-8 Pseudo first-order degradation of PCE in aqueous solutions by sonication for different ethanol fractions ( $C_0 \approx 150 \text{ ppm}$ )

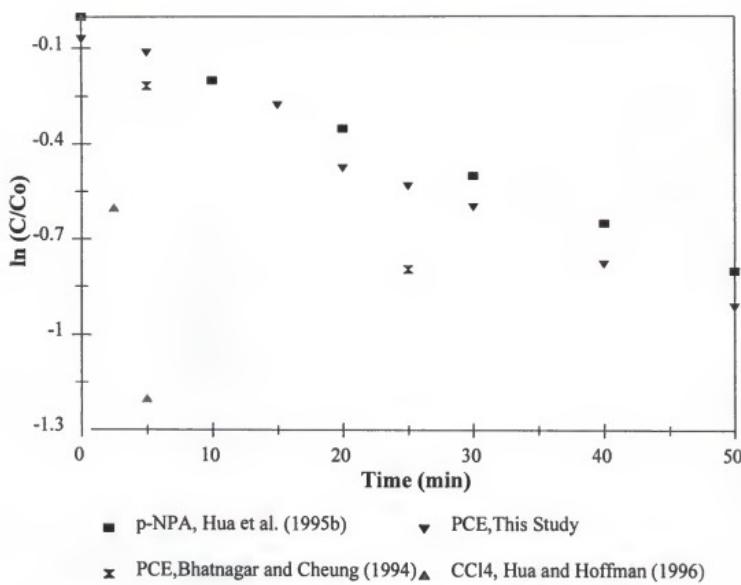


Figure 6-9 Degradation of various compounds by sonication

sonication degradation of PCE solution without ethanol. Data for the sonication degradation of *p*-nitrophenyl acetate (*p*-NPA) provided by Hua et al. (1995b), seen in Figure 6-9, also agreed with the sonication degradation observed in this research. Degradation of carbon tetrachloride (CCl<sub>4</sub>) was reported by Hua and Hoffman (1996) is also included in Figure 6-9. The degradation of CCl<sub>4</sub> under similar sonication conditions seemed to degrade faster than that of the other compounds reported. This could be explained by the single bond configuration in CCl<sub>4</sub>, whereas in the other chemicals either double bonds, PCE, or aromatic bonds, *p*-NPA, had to be broken for dissociation of the chemical to occur. These double and aromatic bonds require more energy to break, which is why it took longer for the these chemicals to degrade under similar sonication circumstances. Levine (1988) reported that to break a Cl atom from CCl<sub>4</sub> would require an energy of 305.9 kJ/mol; to break a bond of H on a phenyl group (as in *p*-NPA) would require 464 kJ/mol; and to break a C=C bond (as in PCE and *p*-NPA) would require 733 kJ/mol. So, while CCl<sub>4</sub> degradation requires cleavage of four single bonds with smaller energy requirements, degradation of *p*-NPA and PCE require cleavage of a larger number of bonds and of more complex bonds.

At constant PCE concentrations, the degradation rate constant decreased with increasing ethanol percentages (Table 6-1). This seemed to indicate that as more ethanol molecules are present in the contaminant solution, less energy was directly available for contact with the PCE molecules. At the relatively low concentrations studied in this research, the ethanol molecules theoretically competed with the PCE molecules for free radicals in solution, and therefore, decreased the rate at which PCE was degraded by the

Table 6-1. First-order degradation rate constants from sonication of PCE aqueous solutions as functions of initial concentration and ethanol percentages.

Initial PCE Concentration	Degradation Rate Constant, $k \cdot 10^3$ (min <sup>-1</sup> )				- Slope (G/EtOH%)
	0 %	10%	30%	50%	
25 ppm	19.32	10.06	4.08	0.42	5.49
50 ppm	16.01	6.41	3.89	0.40	8.00
75 ppm	9.34	5.14	2.14	0.39	12.56
100 ppm	9.13	5.02	2.07	0.38	16.15
150 ppm	8.83	4.65	1.46	0.00	21.36
Slope (G/PCE Conc)	0.0859	0.0592	0.0154	0.0060	

Table 6-2. Half-lives of PCE degrading from sonication of PCE aqueous solutions as functions of initial concentration and ethanol fractions.

Initial PCE Concentration	Half-life, $t_{1/2}$ (hr)			
	0 %	10%	30%	50%
25 ppm	0.598	1.148	2.831	27.83
50 ppm	0.721	1.802	2.969	28.78
75 ppm	1.237	2.247	5.397	29.39
100 ppm	1.265	2.301	5.580	30.40
150 ppm	1.308	2.483	7.911	>33.00

highly oxidizing free radicals. If the concentrations were high, this competition would have been for space in the cavitation bubbles themselves. These results agreed with those of Hua et al. (1995b), who also noted that cosolvent presence decreased the rate of degradation by ultrasonic irradiation. Hua et al. (1995b) stated that a cosolvent may preferentially accumulate at the bubble interface, which takes away potential space for PCE molecules to undergo sonolysis. In this experiment, the large concentration of ethanol (>100,000 ppm for 10%) far exceeded the relatively small amount of PCE in the solution, which allowed them to scavenge the free radicals easily compared to the PCE molecules. The results listed in Table 6-1 showed that for every concentration of PCE evaluated, the higher the ethanol percentage in solution, the lower the degradation rate constant. These decreasing degradation rates as a function of ethanol fractions were displayed on Figure 6-10. These lowering degradation rates resulted in longer degradation times, as evidenced by the increasing PCE concentration half-lives with increasing ethanol percentages (Table 6-2). This trend was also displayed as the relative concentrations (C/Co) of PCE were plotted over the duration of the experiments (Figure 6-11). This trend was seen throughout the experimental evaluations until the 50% ethanol fraction solutions where degradation rates were extremely low, and eventually were negligible for the 150 ppm PCE solution (Table 6-1).

Increasing concentrations of PCE were generally found to have decreasing degradation rates at constant ethanol percentages (Table 6-1). This appeared to indicate that higher amounts of PCE in solution subjected to a constant amount of ultrasonic energy allowed for less energy to fully contact, be absorbed by, and then degrade the PCE

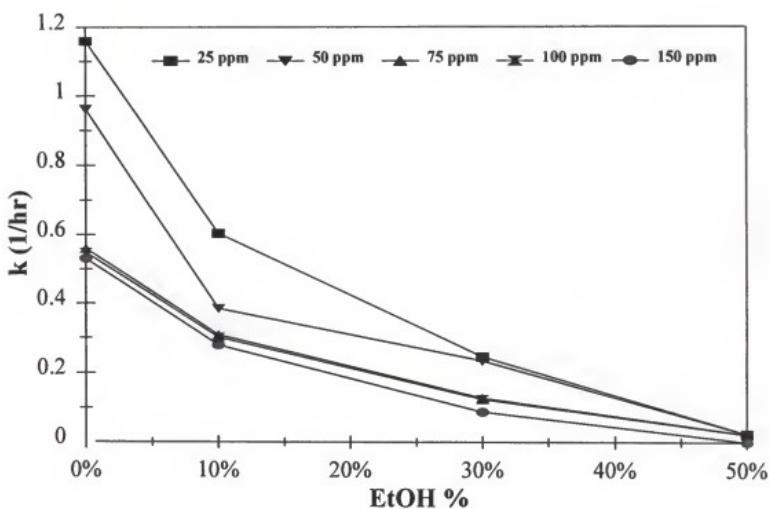


Figure 6-10 Degradation rate constants produced by sonication of aqueous solutions containing PCE at different initial concentrations in various ethanol fractions

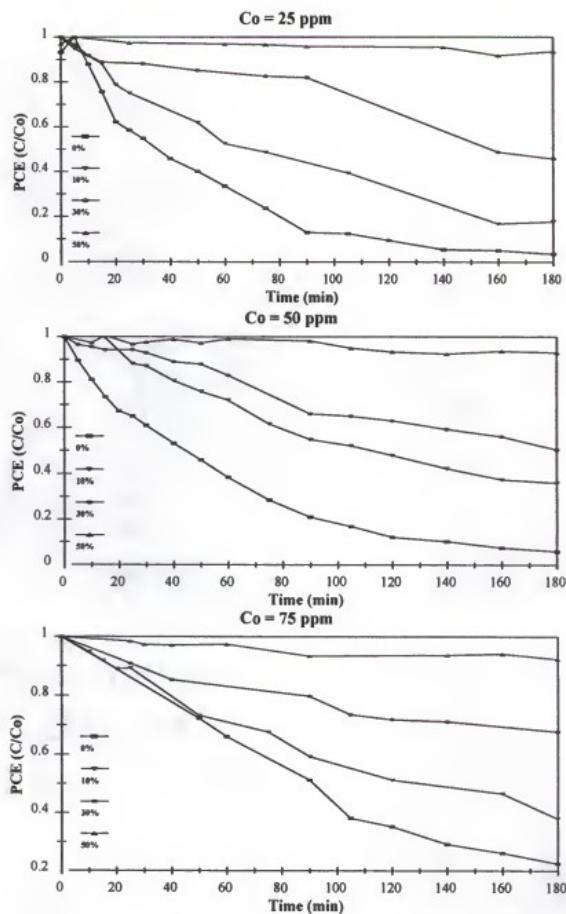


Figure 6-11 PCE (in dimensionless concentration) degradation due to sonication as a function of time at various initial concentrations

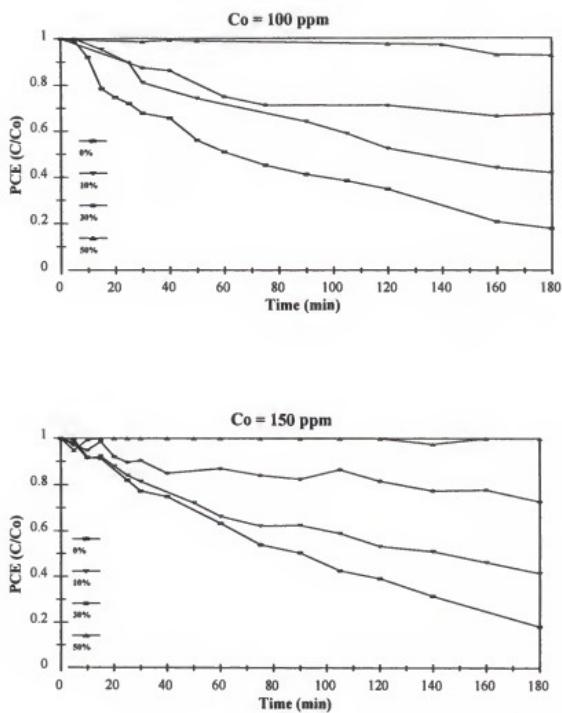


Figure 6-11 contd.

contaminant in the solution at a constant rate. This may have been due to a smaller fraction of the overall PCE in solution was able to scavenge the free radicals in the total solution volume. Subsequently, the half-lives of PCE concentration mirrored this behavior. In Table 6-2, it was also noted that the half-life values for PCE increased with increasing initial PCE concentrations. This trend was further evidenced throughout experimentation on solutions with various ethanol percentages as well.

Ethanol was also seen to decrease over time due to sonication (Figure 6-12). However, the decrease in ethanol was fairly negligible over time due to the large amount that was present as cosolvent fractions in solution. Figure 6-12 displays ethanol at 10%, 30%, and 50% of solution in which PCE was present at 100 ppm concentration. This figure displayed the general behavior of ethanol as a function of sonication in this study. As seen in Figure 6-12, ethanol decreased over time, but not in any discernable pattern. The free radicals most likely oxidized ethanol molecules, but not enough of them to make a significant impact on the overall ethanol concentration.

#### Energy Efficiency

An energy efficiency value (G) was used to evaluate the performance of sonication based on the PCE concentration and energy input into the sonicated liquid (Hua et al., 1995a). This efficiency value was given by Hua et al. (1995a) as:

$$G = \frac{\Delta CN_o V}{\Delta TW} [\text{molecules / kJ}]$$

where  $\Delta C$  is the change in the PCE concentration over a given time interval  $\Delta T$ ;  $V$  is the volume of solution;  $N_o = 6.02 \times 10^{23}$  molecules/mol; and  $W$  is the wall voltage. It was also

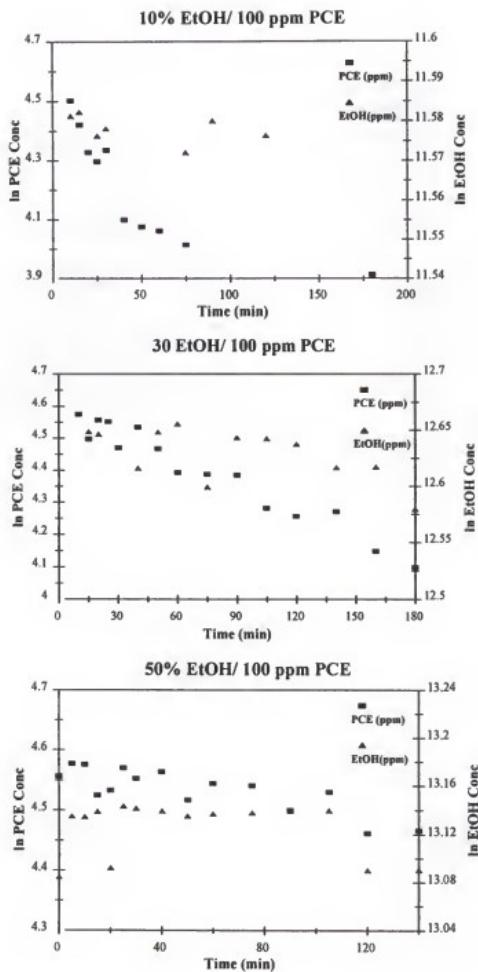


Figure 6-12 Degradation of ethanol and PCE over time due sonication

noted that this G value does not include any other chemical reaction, such as the simultaneous degradation of various possible by-products, but focused on the degradation of PCE. This value basically provided a measure of the ultrasonic energy reaching the PCE molecules in solution, which catalyzed the sonochemical degradation of these contaminant molecules.

The results showed that as the initial solution concentration increases, the G value increased as well (Figure 6-13). This implied that a higher number of PCE molecules subjected to a constant ultrasonic energy amount increased the efficiency value or number of molecules influenced by the energy, as earlier supposed. Although more molecules were in contact with energy applied to the solution, the rate of PCE degradation in the total system volume effectively decreased with increasing PCE initial concentration, as shown by the results. This suggested that the ultrasonic energy was absorbed by the PCE in solution, however, in smaller amounts per molecule due to the energy being distributed to a larger number of molecules in solution. Lower amounts of energy applied to the molecules slowed the degradation of the PCE molecules. This explained why even though energy efficiency increased as PCE concentration increased, the overall degradation rates simultaneously decreased. This trend was followed for every solution at all cosolvent percentages investigated. Slopes of the relationship of G as a function of PCE concentration are listed on Table 6-1. These slopes showed that for increasing ethanol percentages, the difference between the degradation rates of PCE over a range of PCE concentrations decreases. This indicated that the effect of PCE concentration on energy efficiency decreased as ethanol fraction in the solution increases.

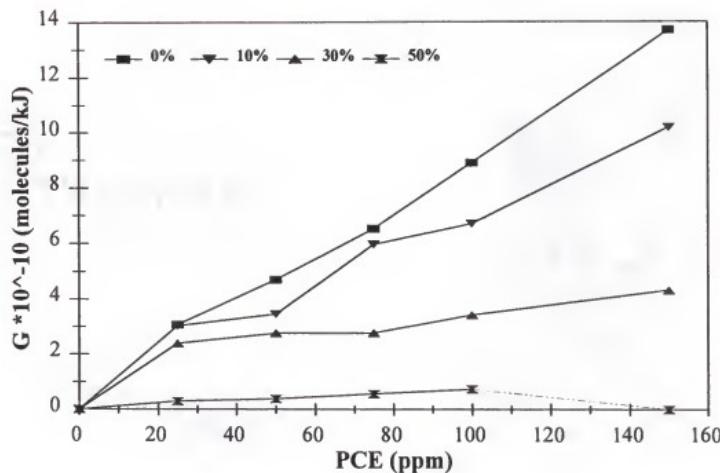


Figure 6-13 Energy efficiency ( $G$ ) of sonochemical destruction of PCE in aqueous solutions which contain various ethanol fractions as functions of PCE concentration

The energy efficiency was also seen to decrease as a function of increasing ethanol percentage evaluated (Figure 6-14). This seemed to validate the earlier deduction that as more ethanol molecules were present in the contaminant solution, less energy contacted and was absorbed by the PCE molecules. This competition of ethanol molecules with PCE molecules resulted in decreased degradation rate constants with increased ethanol percentages in the contaminant solutions studied. This trend was also consistent for every concentration of PCE solution that was evaluated in this research. Slopes of the relationship of G as a function of ethanol are listed on Table 6-1. These values showed that for increasing initial concentrations of PCE, the difference between the degradation rates of PCE over a range of PCE concentrations increases. This indicated that the affect of ethanol on energy efficiency increased as initial PCE concentration in the solution increased.

It was earlier suggested that although the mixing that occurs during sonication may play a role in the degradation of PCE, it is likely a minor one when compared to the overall cavitation process itself. Comparing the degradation rate constant for the stirring setup,  $0.179 \text{ hr}^{-1}$  (Figure 6-3), to the value gathered by experimental sonication of an identical aqueous solution containing PCE (50 ppm/ 0% EtOH, in Figure 6-5),  $0.961 \text{ hr}^{-1}$ , showed that mixing may be responsible for less than one-fifth the degradation due to sonication. These results agreed with the assertions of Suslick (1990) and Hua et al. (1995b) who both stated that the majority of degradation that occurs during sonication is related to the energy generated by the cavitation process, not by direct interaction of the molecular species, which is seen in simple mixing. Intermolecular collisions aided in the

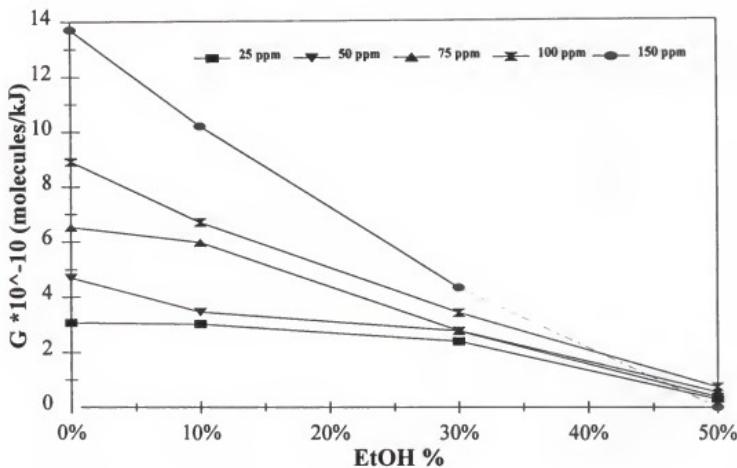


Figure 6-14 Energy efficiency (G) of sonichemical destruction of PCE at multiple initial concentrations in aqueous solutions as functions various ethanol fractions

sonochemical destruction of PCE, but do not dominate the degradation process induced by sonication. So even though the mixing that occurs during sonication could not be exactly duplicated with a stirrer, the data allowed for an appraisal of the role of mixing in sonochemical destruction.

#### Parameters Not Evaluated

Although pH was not measured in this experiment, it is well documented and was expected that pH would decrease over the duration of the sonication experiments due to production of H from sonolytic reactions (Cheung et al., 1991; Kotronarou et al., 1992; Orzechowska et al., 1995; Rajan et al., 1998).

Despite not being measured in this research, chlorine ion was the expected dominant product for sonolysis of chlorinated solution such as PCE (Hua and Hoffman, 1996). However, even if measured, it has been stated that no satisfactory connection exists between degradation rate and the chloride ion mass balance recorded in degradation by sonication (Petrier et al., 1998).

Headspace vapor was not analyzed during the sonication experiments. Even though ultrasonication causes degassing, Hua and Hoffman (1996) stated that in a closed system volatile solutes re-enter the treated solution and the observed losses are due to chemical reaction and not to volatilization. This was supported by the sonication experiment which measured concentration over time in the inactive sonication system (Figure 6-2). In this experiment, no significant concentration loss could be detected from the closed system. Consequently, volatilization losses of PCE were deemed negligible in the system configuration used during the sonication experiments.

### Cost Analysis

Treatment of the PCE waste was quoted to cost \$1.25/gallon by Tim McHale of ManTech Environmental Services Corporation. An estimated waste volume of 20,000 gallons would cost \$25,000 to treat after removal from the site. An estimate of \$15,000 for use of a sonication system in the field was gathered from a personal communication of Dr. Debra Reinhart of the University of Central Florida. A cost of \$0.0544/KWH for electric power to run the sonication system was based on Gainesville Regional Utilities estimates. Using the power to volume ratio of 150 W per 500 mL of solution that was incorporated in the experimental procedure, a power requirement of 22,710 KW per 20,000 gallons was calculated for field scale-up.

Figure 6-15 shows that for most of the PCE solutions, the cost of sonichemical destruction was greater than the \$25,000 that it would cost to destroy the waste containing PCE. As PCE initial concentration and ethanol concentration increased, so did the cost of treatment. Evaluation of the power to volume requirements studied in this research indicated that using sonication to destroy PCE was not economically feasible. However, by adjusting the power to volume ratio and increasing the sonication time of the effluent, the cost of power could be reduced dramatically. Further studies would need to be conducted to determine the power to volume ratios and residence times that might allow for economically feasible use of the sonicator as the primary treatment source of solutions containing PCE in the field.

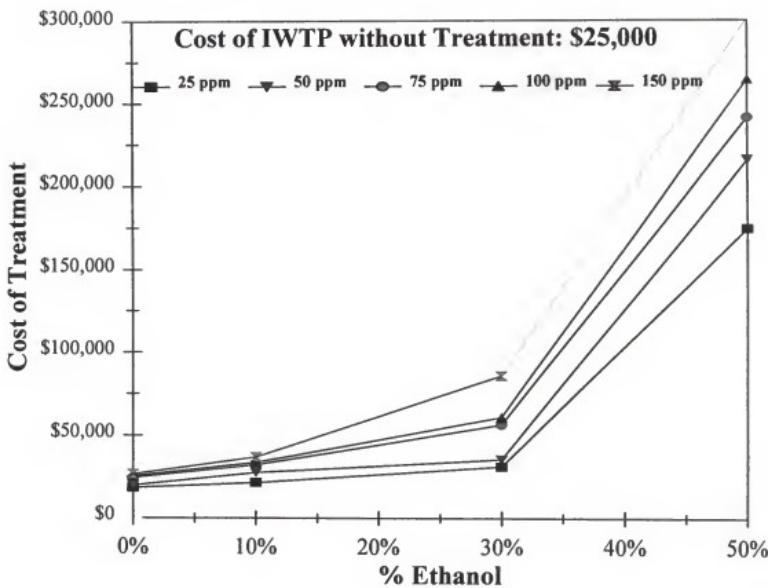


Figure 6-15 Cost analysis of treating solution containing PCE with sonication as a function of the amount of ethanol in solution

### Conclusions

The purpose of this research was to evaluate sonication as a process for degrading PCE contaminated effluents following their removal from subsurface environments under remediation. Various ethanol volumetric percentages were evaluated over a range of initial PCE concentrations to determine how each of these factors might affect the sonication degradation process.

Experimental results showed that sonication is an effective method of degrading PCE in aqueous solutions over time. In addition, these results displayed a pseudo first-order kinetic degradation of the PCE aqueous solutions, which agreed with previous experimental results found in the literature.

Increasing ethanol percentages in the aqueous effluent resulted in decreasing degradation rates of PCE in solution. This implied that the ethanol molecules were in competition with the PCE molecules for the oxidizing free radicals that were produced due to application of sonication energy to the solution volume. This led to a decrease in the rate at which PCE could be degraded by the highly oxidizing species in solution.

Increasing initial concentrations of PCE in solution generally resulted in decreasing degradation rates during the sonication process. This seemed to indicate that higher amounts of PCE in solution were subjected to limited number of free radical species. This may have led to a smaller fraction of the overall PCE in solution to scavenge the free radicals in the total solution volume, which decreased the amount that would degrade.

An energy efficiency value (G) was used to evaluate the performance of the sonication process based on the PCE concentration and energy input into the sonicated liquid. Results showed that as initial solution concentration increases, the G value increased as well. This appeared to indicate that a higher number of PCE molecules being subjected to a constant ultrasonic energy amount increased the efficiency value or number of molecules influenced by the energy.

The energy efficiency decreased as a function of increasing ethanol percentage in the aqueous solution. This result appeared to substantiate the theory that ethanol molecules competed for free radicals, space, and energy with the PCE molecules.

Overall, sonication was seen to degrade PCE in aqueous solutions becoming less effective as cosolvent fraction increased and initial PCE concentrations decreased. Future scale-up experiments are recommended to determine if the effectiveness seen in the lab-scale research results could be duplicated or improved at field scale.

## CHAPTER 7 SUMMARY AND CONCLUSIONS

### Conclusions

The main goal of this research was to determine the effectiveness and efficiency of waste management techniques that can be implemented in the treatment of effluents from in-situ flushing procedures. These technologies took the form of intermediate treatment measures or destructive techniques which previously had not been fully explored. The research focused on management of effluent taken from a surfactant/cosurfactant flush at Hill AFB, Utah, and effluents that might result from cosolvent flushing of a soil contaminated with PCE. The specific conclusions of this research are:

1. Phase separation by addition of a neutral electrolyte (NaCl) to or by increasing ambient temperature of the SPME were found to be effective intermediate treatment methods for decreasing the amount of NAPL-saturated waste potentially targeted for incineration. The optimum separation ratios of aqueous phase volume after separation to total volume previous to separation were ~0.95 for salt addition and 0.96 for increasing ambient temperature.

2. Phase separation by salt addition and increased temperatures resulted in a majority of the NAPL, surfactant, and hydrophobic components partitioning into the separated organic-rich phase. Percentage of pentanol mass partitioning into the organic-rich phase increased with increasing amount of salt added. Also, as ambient temperature increased, less pentanol partitioned into the organic-rich phase.
3. The COD concentrations in the aqueous-rich phases were found to decrease with increasing salt addition and increasing temperatures. It was also found that salt separation reduced the COD load of the effluent by up to 90%, while elevating temperatures reduced it by nearly 80%. The addition of salt at elevated temperatures resulted in a reduction over 90% of the COD load in the aqueous-rich phase. The majority of the COD concentration (~99%) was attributed to the presence of pentanol.
4. Combining salt addition at elevated temperatures reduced the volume of NAPL-dominated waste by over 95%, while >98% of the mass of the targeted hydrophobic components partitioned into the organic-rich phase after separation. For increasing temperatures, lower amounts of salt were required to produce similar levels of volumetric phase separation and the reverse was also found to be true.
5. PCE was found to degrade in the presence of zero-valent iron in a pseudo first-order manner over time for various iron surfaces. Degradation of a higher PCE concentrations with zero-valent iron occurred more slowly than lower PCE concentrations. Increasing

the ethanol fraction in the PCE solutions was found to decrease the adsorption of PCE to the iron surface, and, therefore, to decrease PCE degradation rate regardless of iron surface or concentration level.

6. In degrading PCE, the results showed that the nickel-plated iron (NiFe) was the most effective, followed by the acid pretreated zero-valent iron (TreatFe), and least effective was the untreated zero-valent iron.

7. Sonication was shown to be an effective method for degrading PCE in aqueous solutions and displayed pseudo first-order degradation rates. Increasing ethanol fractions and initial PCE concentrations in the aqueous effluent resulted in decreasing degradation rates of PCE in solution due to sonication.

8. Sonication was observed to degrade PCE in aqueous solutions less effectively as the initial solution concentration decreased and the ethanol fraction in solution increased based on decreased energy efficiency values ( $G$ ). This was likely due to ethanol scavenging the highly oxidizing radicals in solution away from the PCE molecules.

9. Phase separation of SPME and application of iron to solutions containing PCE were found to be cost effective measures of handling effluent waste. Conversely, sonication was not found to be initially cost effective, but with modifications and additional research could be improved to warrant field scale use.

### Recommendations

The waste management techniques discussed in this research could be used to improve remedial operations at hazardous waste sites; however, further work is recommended. Suggested future work includes:

1. Experiments comparing the effectiveness and efficiency of SPME waste effluent phase separation utilizing various electrolytes of different cationic charge strengths and various ambient temperatures, including decreased temperature values.
2. Phase separation experiments utilizing various weight percentages of salt and different ambient temperatures on samples taken throughout more periods during the in-situ flushing experiment.
3. Experiments comparing phase separation of SPME mixtures with various surfactants, different surfactant/cosurfactant combinations, and including diverse NAPL compositions.
4. Experiments to determine the effect of phase separation on different properties of the overall SPME, including the separated aqueous and organic-rich phases. Some of these properties include surface tension, viscosity, density, and water content of separated organic-rich phase.

5. Experiments applying both zero-valent iron and sonication to actual waste effluent from a cosolvent flushing procedure and application of these methods during actual field remediation processes. To conduct experiments which better map the dechlorination pathways for degradation of various chlorinated aqueous solutions.
6. Conducting dechlorination experiments using various other metals, such as palladium, copper, aluminum, etc. and other bimetallic combinations. Observation of the different effects the metal and metallic combinations have on dechlorination in aqueous solutions containing assorted cosolvent mixtures at varying cosolvent fractions.
7. Evaluation of gases produced during dechlorination as a function of time, concentration, sorption surface used, and cosolvent fraction present. Also, evaluation of headspace gas over time during sonication treatment of chlorinated aqueous solutions.
8. Determine sorption site efficiency occurring during dechlorination as a function of time, initial chlorinated organic concentration, and cosolvent fraction. Additionally, employ processes to regenerate metal solids and determine how this would affect their sorption and dechlorination capacity.
9. Conducting sonication experiments employing different methods of applying the energy to solution, such as using parallel-plate configuration. Comparing the energy efficiencies of these various sonication configurations and how they may be modified for

large scale use at contaminated field sites.

10. Determination of how wastes treated using methods explored in this research effect further treatment, disposal, and possible recycle methods.

APPENDIX  
CONTAMINANT CONCENTRATIONS

**IRON DEGRADATION**

	<u>K<sub>i</sub> (cm), (cm<sup>3</sup>/cm<sup>2</sup>)</u>		
	<u>NiFe</u>	<u>TreatFe</u>	<u>Fe</u>
0%	3.277E-05	1.558E-04	1.036E-04
10%	3.404E-05	1.089E-04	9.9172E-05
30%	2.251E-05	1.059E-04	8.6566E-05
50%	1.473E-05	1.023E-04	8.0264E-05

K<sub>i</sub> = concentration independent adsorption coefficient (Kim et al., 1998)

## LNAPL TARGET ANALYTICS

		PXYL (mg/L)	DECANE (mg/L)	TMB (mg/L)	DCB (mg/L)	UNDEC (mg/L)	DODEC (mg/L)	TCB (mg/L)	NAPHTH (mg/L)	TRIDE (mg/L)	PENTANOL (mg/L)	Brij 97 Peak Ratio
Salt W%	Phase, Time											
5	Oil, IPV	57.30	243.80	200.20	57.80	528.60	326.90	283.50	28.40	119.60	92100	0.5981
6	Oil, IPV	138.30	501.20	455.90	152.10	1245.20	766.80	602.20	17.60	292.10	149583	1.4339
7	Oil, IPV	184.30	660.10	602.20	319.00	1687.70	1020.90	836.30	41.00	313.30	207189	1.6966
8	Oil, IPV	192.30	681.60	614.70	312.40	1726.50	1043.70	828.70	20.00	298.90	292000	1.6772
9	Oil, IPV	235.80	845.20	777.20	422.50	2197.50	1327.00	1037.20	34.60	378.80	403000	2.1849
10	Oil, IPV	220.30	794.90	720.30	362.80	2020.50	1188.40	986.90	37.80	340.90	390000	1.9982
11	Oil, IPV	225.50	818.40	742.40	389.20	2088.90	1204.30	995.80	34.10	463.80	416000	1.94
12	Oil, IPV	240.20	862.30	785.70	235.90	1765.90	1308.60	1066.80	59.70	359.80	454000	2.1637
13	Oil, IPV	246.20	876.40	804.70	411.00	2246.50	1364.30	1132.30	61.60	556.60	461000	2.2033
14	Oil, IPV	226.60	816.40	747.40	386.80	2101.30	1262.80	1050.10	71.60	608.50	452000	2.1084
16	Oil, IPV	341.40	1207.30	1111.00	562.50	3118.70	1845.00	1519.10	102.60	815.80	694000	2.962
20	Oil, IPV	348.60	1259.60	1149.80	610.10	3210.90	1952.10	1520.70	43.30	575.70	695000	2.9594
	Aqueous, IPV	—	0.14	—	0.01	0.85	0.33	0.31	0.16	0.01	17300	0.4916
6	Aqueous, IPV	—	0.19	—	—	0.92	0.34	0.30	0.20	0.13	13800	0.0991
7	Aqueous, IPV	—	0.26	—	0.01	1.00	0.44	0.35	0.10	0.22	10700	0.0247
8	Aqueous, IPV	—	0.26	—	—	1.15	0.43	0.41	0.16	0.17	8740	0.03
9	Aqueous, IPV	—	0.30	0.01	—	1.20	0.46	0.45	0.30	0.27	6810	0.0282
10	Aqueous, IPV	—	0.79	—	—	0.83	1.26	1.04	0.12	0.54	6780	0.0454
11	Aqueous, IPV	—	0.33	—	—	1.71	0.69	0.50	0.01	0.24	5170	0.0331
12	Aqueous, IPV	—	0.49	—	—	1.44	0.73	0.50	0.12	0.24	5280	0.0223
13	Aqueous, IPV	—	0.28	0.10	—	1.08	0.43	0.33	0.14	0.25	3780	0.0335
14	Aqueous, IPV	—	0.25	—	0.00	1.26	0.59	0.47	0.17	0.24	3930	0.0366
16	Aqueous, IPV	—	0.25	0.02	—	0.88	0.25	0.27	0.15	0.14	3380	0.0356
20	Aqueous, IPV	—	0.17	—	—	0.70	0.23	0.23	0.20	0.14	2340	0.0313
	Oil, Comp	—	—	—	—	—	—	—	—	—	—	—
6	Oil, Comp	—	7.40	8.30	0.10	45.90	35.20	29.60	1.30	17.30	23092	0.2398
7	Oil, Comp	7.30	91.60	103.70	14.20	387.00	216.50	231.60	11.40	120.50	128519	1.898
8	Oil, Comp	9.40	135.60	141.00	19.20	570.10	300.30	321.80	12.90	124.90	181674	2.5956
9	Oil, Comp	6.50	128.90	130.60	16.50	493.00	277.20	311.90	16.50	149.70	18049	2.5071
10	Oil, Comp	7.60	130.30	134.40	17.80	563.80	336.40	304.20	13.80	101.50	193948	2.5319
11	Oil, Comp	13.80	194.00	194.90	29.40	809.20	436.40	456.80	27.30	229.40	309287	3.5152
12	Oil, Comp	11.90	158.60	162.20	22.00	714.70	364.60	377.20	13.00	127.50	270829	3.1056
13	Oil, Comp	11.20	149.50	168.80	22.00	776.80	379.80	406.00	20.40	202.70	285955	3.2483
14	Oil, Comp	11.20	152.30	170.60	21.20	829.80	395.30	399.90	18.30	151.10	291046	3.2336
16	Oil, Comp	12.70	179.30	185.10	23.20	864.60	401.70	427.90	24.80	217.20	331707	3.5132
	Aqueous, Comp	0.2	2.73	0.33	0.1	1.22	0.49	0.07	0.1	0.37	95.96	—
7	Aqueous, Comp	—	0.02	0.05	—	—	0.09	0.06	0.04	0.13	9594.16	0.0268
8	Aqueous, Comp	—	0.12	0.03	—	0.59	0.22	0.16	0.11	0.15	7680.50	0.0185
9	Aqueous, Comp	—	0.07	0.05	0.01	—	0.09	0.06	0.07	0.11	6657.82	0.0138
10	Aqueous, Comp	—	0.08	0.03	—	0.39	0.14	0.14	0.11	0.11	4832.39	0.0315
11	Aqueous, Comp	—	0.1	0.06	—	0.06	0.14	0.17	0.27	0.1	4558.87	0.0333
12	Aqueous, Comp	—	0.08	0.03	—	0.03	0.07	0.07	0.03	0.09	3839.40	0.0135
13	Aqueous, Comp	—	0.08	0.04	—	0.15	0.1	0.06	0.12	0.09	3265.79	0.0165
14	Aqueous, Comp	—	0.02	0	0.01	—	0.07	0.07	0.03	0.03	2554.13	0.0133
16	Aqueous, Comp	—	0.06	0.01	—	0.05	0.07	0.14	0.09	0.09	2643.77	0.0133
	SFME, IPV	11.42	44.27	34.05	0.29	81.11	58.89	43.99	2.80	17.17	17400.00	1.00
	SFME, Comp	1.28	11.52	11.20	0.04	35.70	23.63	21.07	1.61	7.26	25200.00	1.00

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### BIOGRAPHICAL SKETCH

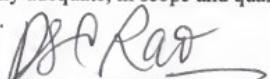
Clayton J. Clark II was born in Chicago, Illinois, on July 31, 1971. He graduated from Florida A&M University High School in Tallahassee, Florida, in 1989. He then attended Florida A&M University in Tallahassee and graduated with a Bachelor of Science degree in chemical engineering and minor degrees in mathematics and chemistry. He continued his education at the University of Florida, where he received a Master of Engineering degree in environmental engineering sciences in August 1995. He then began working toward a Ph.D. degree in environmental engineering sciences at the University of Florida. Upon graduation, the candidate will continue to participate in research and teaching on the university level.

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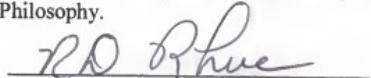
Michael D. Annable, Chairman  
Associate Professor of Environmental  
Engineering Sciences

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P. Suresh C. Rao, Co-Chairman  
Graduate Research Professor of Soil and  
Water Science

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R. Dean Rhue  
Professor of Soil and Water Science

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Paul A. Chadik  
Assistant Professor of Environmental  
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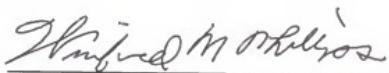


Joseph J. Delfino

Professor of Environmental Engineering  
Sciences

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy

May 1999



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Winfred M. Phillips

Dean, College of Engineering

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M. J. Ohanian  
Dean, Graduate School